The solubility of dental luting cements -a combined in vivo/in vitro investigation-

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THE SOLUBILITY OF DENTAL LUTING CEMENTS

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L.J. Pluim

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Stellingen behorende bij het proefschrift
"THE SOLUBILITY OF DENTAL LUTING CEMENTS"

I

De klinische voorspelbaarheid van het desintegreren van cementen door middel van de ADA specificatietest is van nul en gener waarde.

dit proefschrift.

II

Het oplosbaarheidsverloop van bevestigingscementen is -zowel in vitro als in vivo- in de tijd gemeten lineair.

dit proefschrift.

III

Er is geen correlatie tussen de buffercapaciteit van het speeksel en de oplossnelheid van bevestigingscement in een mond.

dit proefschrift.

IV

Het raderen van het werkmodel ter plaatse van een brugtussendeel om een beter esthetisch resultaat te verkrijgen, moet worden ontraden.

Käyser, A.F. Over de aanpassing van de gingiva aan de pontic.
Ned. Tijdschr. Tandheelkd. 85: 71, 1978.

V

Voor het verkrijgen van een stabiel eindresultaat is het noodzakelijk een occlusie-analyse uit te voeren vóór, maar zeker ná orthodontische behandeling.

VI

Bij het presenteren van de wereldprimeur betreffende cariës in een niet doorgebroken element gaan Baab et al. ten onrechte uit van de premisse "unerupted"

Baab et al. Caries and periodontitis associated
with an unerupted third molar.
Oral Surg. 58: 428, 1984.

VII

De conclusie van Jostes en Holland, dat er geen relatie bestaat tussen het occlusaal inkorten van een element en post-endodontische bezwaren, is onjuist.

Jostes, J.L. & Holland, G.R. The effect of occlusal reduction after canal preparation on patient comfort.
J. Endodon. 10: 34, 1984.

VIII

De waardering van de tandheelkundige professie voor de volledige gebitsprothese is groter dan blijkt uit het aantal publicaties in de nederlandstalige vakliteratuur, gedurende de laatste vijf jaar.

IX

In de uitdrukking "een extractierijp gebit" komt een in de tandheelkunde veelvuldig gemaakte denkfout tot uiting: na het afnemen van de anamnese wordt de te verwachten therapie als diagnose betiteld.

X

Een proefschrift is geen leerboek.

XI

De academisering van de tandheelkunde is sneller verlopen dan die van het tandheelkundig onderwijs.

XII

Elke schutter is nog geen jager; wel zijn sommige jagers schutters.

XIII

Het eerste wat men na het openen van een verpakking weggooit, is de gebruiksaanwijzing.

Rijksuniversiteit te Groningen

THE SOLUBILITY OF DENTAL LUTING CEMENTS
- a combined in vivo/in vitro investigation -

PROEFSCHRIFT

ter verkrijging van het doctoraat in de geneeskunde
aan de Rijksuniversiteit te Groningen
op gezag van de Rector Magnificus Dr. E. Bleumink
in het openbaar te verdedigen
op woensdag 3 april 1985 des namiddags te 16.00 uur

door

Laurens Johannes Pluim

geboren te Emmen

krips repro meppel

Promotores: Prof. Dr. J. Arends
Prof. Dr. A.C.M. van de Poel

Paranymfen: Th.B.F.M. Gelhard
J.D. Stenvers

De beste wijze om iets te leren,
is er les in te geven.

Seneca

Cover:
scanning electron microscope photograph of a replica taken from six cement samples after 51 weeks in vivo (13x)

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H. Flanderijn

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CONTENTS

CHAPTER ONE

INTRODUCTION AND AIMS OF THE INVESTIGATION

1.1. DENTAL CEMENTS

In dentistry cements are used for various completely different purposes. Historically a typical application is the filling cement; this restorative use, however, became increasingly less important after the development of products with a completely different chemical composition, the so-called "composites".

A second much more important application of dental cements is that as luting agent for securing cast restorations.

Teeth to be restored are partly ground away to create sufficient space for a restoration. An impression of the situation is made and subsequently cast in a model, thus accurately reproducing the oral situation.

When the restoration is ready to be positioned in the mouth the two components of the luting cement (powder and liquid) are mixed and the resulting creamy paste is painted on the prepared teeth as well as inside the restoration. The inlay, crown or bridge is then placed upon the preparation and seated under pressure until the cement has hardened.

Cements are also used as a temporary filling or as a base underneath a restoration. In both cases the aim of the application is to protect the dental pulp against chemical and/or thermal insults. These last two applications are not of interest for this investigation since in the first case the cement has to function for a limited period only, while in the second case the material is not in contact with the oral environment.

From the preceding part it is obvious that the main application of dental cements is as luting cement. Therefore, we will consider this application in more detail.

1.2. LUTING CEMENTS

Zinc phosphate cements have been used in dentistry to secure cast restorations for about 100 years. Originally concocted by Peirce in 1879, this cement consists of a powder and a liquid respectively zinc oxide and phosphoric acid solution. Another cement, used for filling purposes only due to its heavier consistency, and thus unsuitable as a luting cement, consisted of the same liquid and a powder consisting mainly of aluminum silicate. After mixing and hardening the result is the so-called silicate cement. This application is mentioned here because it fits logically in the scheme presented below (Table 1.I), and had consequences for later developments.

Table 1.I. Compiles the four possibilities for the two liquids and the two powders mentioned.

liquid \ powder	zinc oxide	aluminum silicate
phosphoric acid	zinc phosphate cement(1879)	silicate cement(1910)
polycarboxylic acid	polycarboxylate cement(1968)	glass ionomer cement (1972)

Historically there was no real development in dental cements for nearly a century. In 1968, however, a new kind of cement was produced by D.C. Smith using zinc oxide as powder but polycarboxylic acid solution as the liquid component.

The advantages of this cement will be discussed later on in this chapter.

In 1972 Wilson and Kent for the first time mentioned the so-called "glass ionomer" cement, consisting of aluminum silicate and polycarboxylic acid.

1.3. PHYSICAL PROPERTIES OF DENTAL CEMENTS

Since zinc phosphate cement neither adheres to restorations nor to dentine, its "retention" is based only on mechanical interlocking of surface irregularities and is therefore proportional to its compressive strength. This strength, being in the range of 800-1000 $kg.cm^{-2}$, is enough to give satisfactory clinical results. The disadvantage of this type of cement is its initial pH being about 1.6 just after mixing and rising to about 6.0 after a few hours. The acidity causes considerable irritation of the dental pulp that can lead to pulp inflammation.

Another problem of this type of cement is its disintegration in due time, leaving a narrow gap between restoration and tooth. This gap can have as consequence bacterial influx and subsequent irritation of the gingiva and pulp. Disintegration is a result of a combination of pure solubility and mechanical erosion. This process can be delayed by improving resistance against mechanical erosion and/or improvement of solubility characteristics.

Polycarboxylate cement as introduced by Smith (1968) claimed with respect to zinc phosphates:

1. adherence to dentine;
2. better biocompatibility, having a more favorable pH;
3. lower solubility.

Clinical experience, however, showed that the adherence to dentine of polycarboxylate cements could not be relied upon as a main retention mechanism. Better compatibility with respect to the dental pulp could be demonstrated (Plant, 1970). The solubility of polycarboxylates, measured in vitro as described in the ADA-specification test, was found to be less than for zinc phosphate cements.

The newest cement, the glass ionomer type, claims the same advantages, especially its biocompatibility (Pameijer, 1981; Roulet, 1980), a high compressive strength and a slow F^- release, protecting the adjacent dental tissues against secondary caries.

1.4. AIMS OF THIS INVESTIGATION

The aims are:

1. to develop and test a method to measure the chemical solubility of dental cements **in vitro** as a function of time;
2. to develop and test a method to measure the disintegration of dental cements **in vivo** as a function of time;
3. to find possible correlations between 1 and 2;
4. to obtain more insight in the cement disintegration mechanism in vivo.

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CHAPTER TWO.

LITERATURE SURVEY OF CEMENT SOLUBILITY IN VITRO AND IN VIVO

2.1. HISTORY.

More than half a century ago on may the 29th 1933 at four o'-clock in the afternoon, Egbert van Dalen obtained his PhD in the technical sciences at the Technical University in Delft, the Netherlands, on a thesis "Oriënteerende onderzoekingen over tandcementen" (Basic investigations on dental cements). This is the oldest dissertation on dental cements in the Netherlands. The one by Friedrich in 1927 is probably the oldest in Europe on this subject. Little is known about the latter; Van Dalen had serious doubts about the quality of Friedrichs' work because he made his cement samples in Göttingen and did not mention how he stored them until the measurements done later in Breslau.

Van Dalen did extensive chemical-analytical research on cements -among others- zinc phosphate and silicate cements. He performed qualitative and quantitative analysis, gave a microscopic description of the hardening process and explained the influence of the composition on the physical properties.

His most important conclusions were:

1. The hardening reaction of zinc phosphate cement is based on the formation of a tight network, consisting of thin needles of secondary zinc phosphate.
2. The aluminium phosphate present in the cement forms a gel around the zinc oxide particles, retarding the hardening process as well as improving the plasticity.
3. The same aluminium phosphate also enhances the resistance of the cement against acids but promotes the detoriation by alkaline fluids.

As mentioned in Chapter One, the new developments came in 1968 with the introduction of polycarboxylate cement by Smith and in 1972 when Wilson and Kent introduced glass ionomer cements.

2.2. THE VALIDITY OF THE SOLUBILITY TEST OF THE AMERICAN DENTAL ASSOCIATION (ADA) SPECIFICATION.

The American Dental Association (ADA) specification no. 8 for dental zinc phosphate cement prescribes the use of a circular cement specimen of 20 mm diameter and 1.5 mm thick. After hardening for one hour in 100% relative humidity at 37°C, the specimen is placed in a weighing bottle containing 50 ml distilled water. After storage for 23 hours at 37°C the specimen is removed. The water is evaporated from the bottle, and subsequently dried to constant weight at 150°C. After cooling to room temperature in a desiccator, the weighing bottle and contents are weighed. The difference between the final weight of the weighing bottle and its initial weight is considered to be the amount of cement disintegration.

As far as physico-chemical research on cements is concerned, extensive and excellent work has been done during a range of projects throughout the years by the team at the Laboratory of the Government Chemist in London. Starting on this subject in 1970 (Wilson et al.) with zinc phosphate cements, they concluded that in **water** zinc phosphate cements dissolve slower than silicate cements, but that in an **acid** environment the situation is the opposite; the latter most likely resembling oral conditions. Wilson and collaborators found experimentally that a simple specification test is not suitable for a comparison of a zinc phosphate and dental silicate cement on account of the brevity of the test period and a neglect of the pH factor. The limitations of the test for solubility and disintegration in specifications for dental cements have been published by Wilson (1972). The ADA test for solubility and disintegration, although intended as a performance test, is frequently used to evaluate new products and to compare them with existing ones.

In this context the limitations of the test have to be realized. It is assumed that valid information on cement disintegration can be estimated adequately by **weighing** the residues after evaporation. This assumption is not always valid. The disintegration of a cement may produce insoluble products that adhere to the cement specimen, or there may be water-soluble substances in the cement, contributing to the test result, but not an essential part of the cement matrix and thus give an overestimate of the cement disintegration. The gravimetric method is invalid if the leached material is volatile. The consequences of these limitations are an overestimate of cement disintegration in one case and an underestimate in others.

To partly overcome these difficulties and inaccuracies Wilson et al. suggested in 1974 to abandon the existing gravimetric procedure and replace it with a colorimetric determination of the phosphate leached from zinc phosphate cement during the specification test.

Another aspect that deserves attention is the **amount** of cement needed for the ADA-test, which is much more than the normal amount used clinically. Especially capsulated products contain only sufficient material for one or two restorations, but certainly not enough for a standard test specimen. Wilson (1976) noted that phosphate extraction from a zinc phosphate cement is minimal at pH 5.0 and thus the use of distilled water is undesirable; a buffered test solution would be more appropriate.

Summarizing, a critical evaluation of the ADA-specification test for cements (Wilson, 1976) shows that the limitations are:

1. **the duration of the test is too short;**
2. **the test medium is not comparable to oral fluids;**
3. **there is no aspect of abrasion in the test.**

The ADA-test measures elution of water-soluble material, but the terms solubility and disintegration to describe it are incorrect.

Solubility of a solid defined as a physico-chemical property, can only be applied to the situation where a chemical compound is in thermodynamic equilibrium with its solution. These criteria are not met in this test: equilibrium is in general not attained

nor is a dental cement a simple chemical substance. Furthermore, the ADA-test has only a limited clinical significance because it does not give an indication of the fully hardened cement either in water or in oral fluids. The test relates, therefore, to an early vulnerability to aqueous attack and hardening rate. Long-term extrapolations cannot be made and cement types with different setting reactions cannot be compared. Therefore we have to conclude that the test needs to be supplemented by other tests done on fully hardened cements for longer periods of time and in media that simulate oral conditions.

2.3. IN VITRO CEMENT SOLUBILITY RESEARCH.

In 1972 Wilson and Kent introduced a new translucent cement for dentistry: the glass ionomer cement. A comparison with existing cement systems showed that it had the advantage of increased strength and better biocompatibility, while the surface of these cements exhibited a greater resistance to mild acid attack. The setting reaction gives a hard water-insoluble gel. Because of their criticism and demands (see Chapter 2.2) on the ADA-specification, Wilson et al. submitted this new cement not only to the standard solubility test, but also tested fully hardened cement under acid conditions over longer periods. Subsequently the same tests on zinc phosphate, silicate and polycarboxylate cements were applied and all surfaces were studied by scanning electron microscopy. The combined results were compiled by Kent, Lewis and Wilson (1973).

The main conclusions were:

1. Glass ionomer cement combines certain favourable properties of both the dental silicate and polycarboxylate cements.
2. Compared to silicate cement, the glass ionomer cement has a superior surface.
3. Surface integrity is maintained against both aquaeous and weak acid attack.

Subsequently extensive studies were started, ranging from compressive strength through the effects of the powder/liquid ratio,

the polyacid concentration, molecular weight, tartaric acid concentration and a study of erosion in neutral and acidic media. This resulted in a series of papers and is probably the most thorough investigation ever done on any kind of dental cement. Finally research was concentrated on the erosion factor because an important limitation of dental cements is their tendency to erode in oral fluids. Total erosion was described as being the combination of dissolution together with disintegration (Crisp et al., 1980).

All dental cements were subsequently investigated: zinc polycarboxylate cements (Crisp et al., 1976), glass ionomer cements (Crisp et al., 1976, 1977 and 1979) and silico-phosphate cements (Wilson et al., 1982).

In vitro solubility research on luting cements has confined itself to a repetition of the ADA-specification-test, done on new cements with one or more clinically proven brands as controls (Klötzer et al., 1970). Some investigators limited themselves to one type of cement (Bertenshaw et al., 1979; Tomioka, 1981; McCabe, 1979; Theuniers et al., 1982; Matsuya, 1983; Finger, 1983) but nearly all investigators had doubts about the validity of the ADA-test and used different methods (Mesu, 1982) or started to vary test circumstances by using longer periods and/or other pH levels (Eichner, 1968; Valcke, 1975; Azuma, 1982), artificial saliva (Anzai et al., 1977), refreshing the test fluids (Schwickerath, 1982) and agitation (McCabe, 1982) (see Table 2.I).

The variations just mentioned had remarkable effects on the outcome of the tests. While firstly solubility seemed to decrease exponentially with time (Eichner, 1968), it increased when the test fluid (even water) was repeatedly refreshed. Even simple agitation during the test caused a 4 fold increase in solubility (McCabe, 1982). It was also considered possible that under static conditions the disintegrated surface layer acts as a passivating layer and was removed by agitation. **Acid test conditions gave even solubility results which were completely the opposite from results gained in distilled water!**

Smink and Arends (1980) described a new set-up that allowed in vitro measurements of solubility and erosion. In this method the specimens are placed in a continuous stream of test liquid and specimen thickness measured after various periods. The results show that the combined solubility/erosion in a liquid flow results in different relative detoriation rates than in a non-flowing medium.

In 1983 Beech and Bandyopadhyay described exactly the same apparatus (into even the smallest details) but claimed it to be "new" and conveniently left Smink and Arends from their reference list.

2.4. IN VIVO CEMENT SOLUBILITY RESEARCH.

In vivo solubility research on dental cements did not start as a circumscript research project in itself but gradually developed from in vitro studies done by Norman, Swartz and Phillips, starting in 1957.

It continued with additional solubility studies -still in vitro- with other, mostly buffered acid test solutions, longer periods and refreshing the test liquids periodically (Norman et al., 1959, 1963). Finally Norman (1969) started in vivo research and filled relatively large windows on the lingual sides of lower frame prostheses, worn during 30 days by 8 patients. Every few days the appliances were weighed and the loss of cement calculated in $mg.cm^{-2}$. Silicate cement proved nearly insoluble in this period. The loss of zinc phosphate cement varied from 5 to 30 $mg.cm^{-2}$, according to the patient, and of zinc oxide eugenol cement 20 to 100 $mg.cm^{-2}$.

Accuracy was only mentioned as far as weighing the empty appliance was concerned (0.2 $mg.cm^{-2}$). Plaque adherence was "wiped away" and there is no information about possible water resorption.

Variation between patients turned out to be very high, but the disintegration rate per patient was fairly constant. Curiously however was that a temporary cement, a filling material and a luting cement were compared. A more adequate experiment was car-

ried out by Richter and Ueno (1975). They filled holes (approximately 3 mm diameter, 2 mm deep) in the pontics of bridges with a silicophosphate, a zinc phosphate, a zinc polycarboxylate and a zinc oxide eugenol - EBA cement. Impressions of the cement surfaces were made at the start and after one year, silver-plated and photographed. Ranking was done by comparison. Silico-phosphate cement was found to be the most durable cement followed by zinc phosphate cement; the two other cements ranked even.

Osborne (1978) filled small holes (0.82 mm diameter, 1.5 mm deep) in crowns of 15 patients with the same cements and measured cement loss directly with a micrometer after six months, without mentioning accuracy. A marked difference in rate of detoriation of the cements in individual patients was observed. The average depth of loss was 7.6 µm for silico-phosphate cement, 43 µm for polycarboxylate cement and 127 µm for zinc phosphate cement; zinc oxide eugenol cement disappeared nearly completely.

Mitchem and Gronas (1978) placed the same cements **plus** for the first time a glass ionomer cement in sample holders with holes (2 mm diameter, 2 mm deep), fitted in dentures and worn by 10 patients. After six months an impression of the sample holder surface was made and measured directly with a micrometer. Again (as in the two previously published studies) it became obvious that some patients produced a much larger cement loss than others. However, the order of loss within each patient also remained fairly constant. Saliva pH values were not determined or considered. The amount of cement lost ranged from 200 µm for glass ionomer cement, 350 µm for a silico-phosphate cement, 600 µm for zinc phosphate cement to 930 µm for polycarboxylate cement; no accuracy measurement was mentioned.

In 1981 they repeated the experiment with more glass ionomer, silico-phosphate and zinc phosphate cements; the outcome was comparable to the 1978 study.

Glass ionomer and silico-phosphate cements continued to demonstrate reduced solubility under oral conditions when compared to zinc phosphate cements.

Sidler and Strub (1983) tested two glass ionomer and one zinc phosphate cement by filling small holes (0.8 mm diameter, 3 mm deep) in mesio-occlusal inlays on wisdom teeth with these ce-

ments. These teeth were extracted after 14 months and the depth of the holes calculated by measuring three points on the edge of each hole and three points on the bottom (i.e. the cement surface) with a probing tip. Information on accuracy and reproducibility was not given. The results showed again a marked patient variation and a standard deviation of over 100%. The mean value for zinc phosphate cement lost was 500 µm, for one brand of glass ionomer cement 100 µm and 40 µm for the other.

Finally, Mesu and Reedijk (1983) compared one zinc phosphate, one polycarboxylate, one fortified zinc oxide eugenol and two glass ionomer cements in vitro as well as in vivo. In this study, round plane-parallel glass plates (7 mm diameter) were cemented upon stainless steel bottom plates. The thickness of the cement layer exposed to the oral environment was approximately 20 µm. Here the zinc oxide eugenol showed the highest and the glass ionomers the lowest dissolution rates.

Most recently Theuniers (1984), in a thesis on durable sealing by five dental luting cements, described the cementation of enamel cylinders into metal containers with calibrated cement layers of 25 and 100 µm. At several intervals a specimen was taken out, cut into parts, and the cement dissolution measured. Fortified zinc oxide eugenol cement was consistently least resistant, followed by zinc phosphate cement. Glass ionomer cements showed the greatest resistance to dissolution.

From a clinical point of view it would be most realistic to measure the dissolution of cement underneath a cast restoration. Unfortunately, as the solubility also depends on shape, depth, fluid transport etc., it is not possible to reproduce this situation and measure longitudinally in time. Such a measurement technique has to be destructive. Therefore, to make quantitative measurements possible, another method, as will be described in the next chapter, was chosen for this investigation.

TABLE 2.I. SURVEY OF IN VITRO CEMENT SOLUBILITY RESEARCH.

reference	cement type	circumstances	solubility/material loss	after
Eichner 1968	silicate zinc phosphate	water refreshed after 1, 2, 4, 8, 16 days	silicate 1.5 - 2.0% zinc phosphate 0.25 - 8.0%	1, 2, 4, 8, 16 days
Wilson 1970	zinc phosphate	fully hardened cement pH 3.5 - 9.0	mg P_2O_5/disk 8-1	23 weeks
Kent 1973	glass ionomer silicate	pH 4	0.1% - 3.0% 0.8% - 3.9%	1 - 7 days
Wilson 1976	zinc phosphate	small specimens, pH variation, colorimetry	minimum solubility at pH 5.0	24 hours
Wilson 1976	zinc phosphate	pH 4 - 7	mg PO_4/gm cement pH 7 - 0.62 pH 6 - 1.46 pH 5 - 4.08 pH 4 - 10.04	24 hours
Anzai 1977			H_2O pH 4 pH 9	7 days
	zinc phosphate polycarboxylate silicate	pH 4 pH 9	10 1500 4) $mg.cm^{-2}$ 30 1000 11) per day 15 77 27)	
Iwaku 1980	zinc phosphate polycarboxylate	dist.water/lactic acid pH 4	0.10/2.27) $mg.cm^{-2}$ 0.07/2.23)	7 days
Smink & Arends 1980	silicate glass ionomer zinc phosphate polycarboxylate	stream of test liquid erosion pH 2.4	0.02 - 0.75) 2.80) loss of thickness in mm 4.60) disappeared	3 days
McCabe 1982	glass ionomer	agitation	4-fold increase	
Schwickerath 1982	zinc phosphate polycarboxylate zinc oxide-eugenol	metal cylinder cemented in calibrated hole fresh water every 2 min.	20 µm) 75 µm) margin depth 100 µm)	22 months

TABLE 2.II. SURVEY OF IN VIVO CEMENT SOLUBILITY RESEARCH.

Author	test conditions	solubility results
Norman et al. 1969	cement in large holes in frame prostheses for 30 days	silicate cement 0 $mg.cm^{-2}$ zinc phosphate cement 5 - 30 $mg.cm^{-2}$ zinc oxide eugenol cement 20 - 100 $mg.cm^{-2}$
Richter & Ueno 1975	cement in holes (Ø 3 mm) in bridge pontics for 1 year	silico-phosphate cement < zinc phosphate cement < polycarboxylate cement < zinc oxide eugenol-EBA cement
Osborne et al. 1978	cement in holes (Ø 0.82 mm) in crowns for 6 months	silico-phosphate cement 7.5 µm polycarboxylate cement 43.0 µm zinc phosphate cement 127.0 µm zinc oxide eugenol cement - disappeared
Mitchem & Gronas 1978	cement in holes (Ø 2 mm) in prostheses for 6 months	glass ionomer cement 200 µm silico-phosphate cement 350 µm zinc phosphate cement 600 µm polycarboxylate cement 930 µm
Sidler & Strub 1983	cement in holes (Ø 0.8 mm) in inlays for 14 months	glass ionomer cement 40 -100 µm zinc phosphate cement 500 µm
Mesu & Reedijk 1983	cemented round glass plates (Ø7 mm) - cement layer 20 µm for 6 months	glass ionomer cement < zinc phosphate cement = polycarboxylate cement < zinc oxide eugenol-EBA cement
Theuniers 1984	cemented enamel cylinders - cement layers 25 µm and 100 µm 16 - 25 weeks	glass ionomer cement < zinc phosphate cement = polycarboxylate cement < zinc oxide eugenol-EBA cement

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CHAPTER THREE

MATERIALS AND METHODS

3.1. GENERAL INTRODUCTION

In this chapter a description of the materials employed, the experimental set-up and the parameters measured is presented.

The experiments are divided in four main parts:

a. In vitro solubility of dental luting cements.
b. In vivo solubility/disintegration of dental luting cements.
c. Physico-chemical studies on the materials employed in experiment b.
d. Measurements on the saliva of patients participating in the clinical experiment b.

In the in vitro experiment a number of cement samples, embedded in perspex, were placed underneath a constant stream of test liquid perpendicular to the surface, thus simulating erosion and chemical dissolution. Another set was placed into a flow of the same test liquid, simulating chemical dissolution.

The pH of the liquid was in due time gradually lowered, and the deminishing sample thickness was taken as a measure for material loss.

In the in vivo experiment cement samples were -embedded in enamel slices- inserted in lower dentures of 10 patients; the patients did wear the prostheses day and night. At certain intervals replicas were made of the cement surfaces, and the amount of material loss determined by means of stereoscopic scanning electron microscopy.

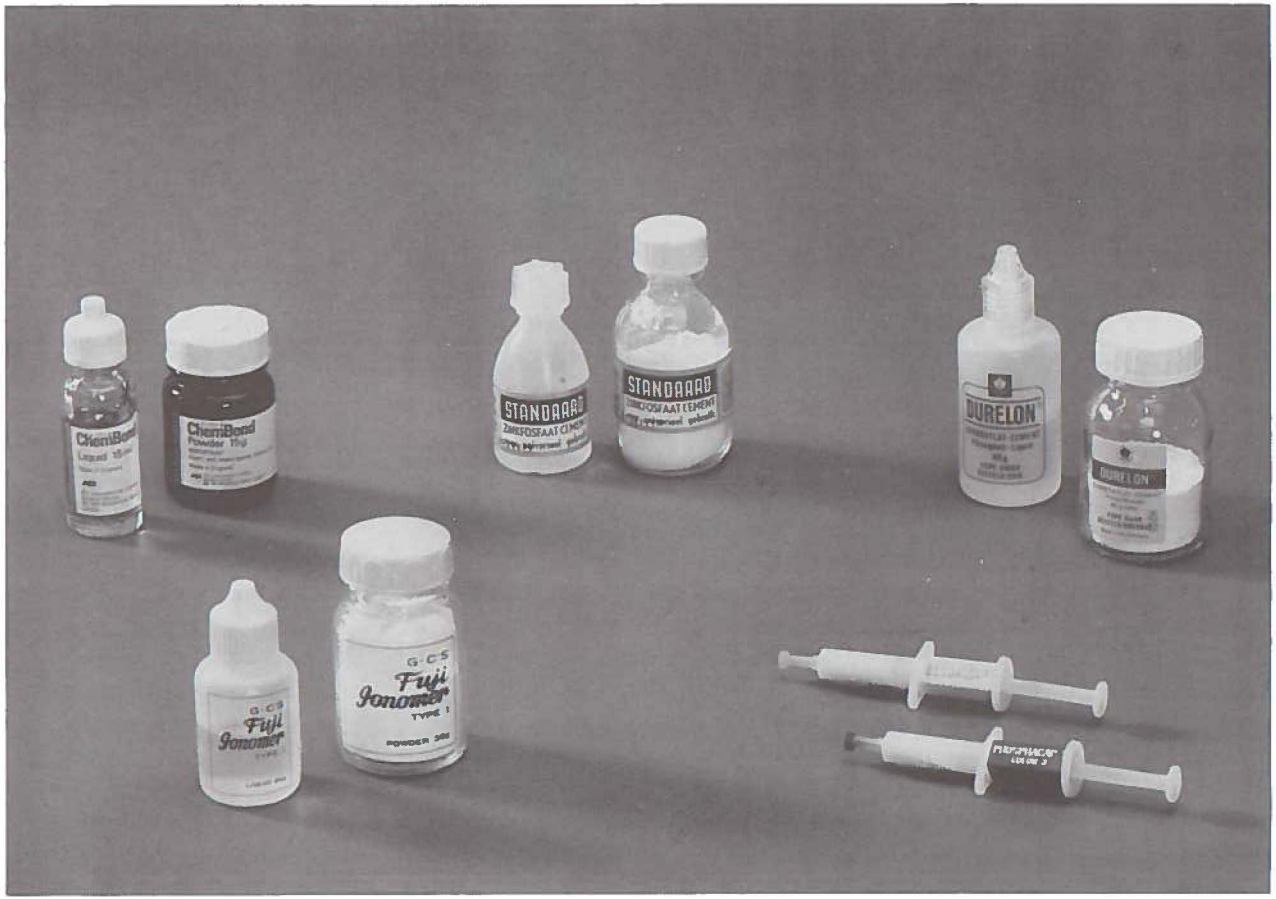

Figure 3.1

Cements tested in the experiments.

3.2. MATERIALS AND STORAGE

3.2.1. CEMENTS

Three types of cement were tested:

1. Zinc phosphate cement;
2. Polycarboxylate cement and
3. Glass ionomer cement.

Two brands of each type most widely sold in the Netherlands were investigated. For brands, manufacturers and batch numbers see Table 3.I and Figure 3.1.

Glass ionomer cements were relatively unknown at the start of the study, especially as luting cement.

Table 3.I. Cements investigated.

Material	Brand	Manufacturer	Batch nr.	Remarks
Zinc phosphate cement	I Standaard	Standaard/ The Netherlands	Powder 1318 Liquid 1019	
	II Phosphacap	Vivadent/ Liechtenstein	Expiration date: march 1984	Encapsu-lated
Polycarboxy-late cement	III Durelon	Espe/ Western Germany	Powder PH 26608 Liquid LH 1047 D	
	IV Bondalcap-C	Vivadent/ Liechtenstein	Expiration date: january 1984	Encapsu-lated
Glass ionomer cement	V Chem Bond	De Trey/ England	Powder ZF118 81/06 Liquid BN YH2 YM	
	VI Fuji	GC Corporation/ Japan	Powder 110521 Liquid 100521	

3.2.2. STORAGE AND MANIPULATION

All cements were stored at room temperature ($\pm$ 20^{o}C). The cements were mixed according to the manufacturers instructions and with each cement one hole of a sample holder (see Figures 3.2 and 3.9) was filled. During setting the sample holder was placed between glass slides in a clamp for 10 minutes; subsequently the samples were stored at room temperature in 100% humidity for about two weeks.

3.2.3. SAMPLES AND SAMPLE HOLDERS

3.2.3.1. IN VITRO EXPERIMENT

The cement specimens were embedded in polymer disks, perforated in the centre, so that the cement sample was 5 mm thick and 3 mm in diameter (see Figure 3.2).

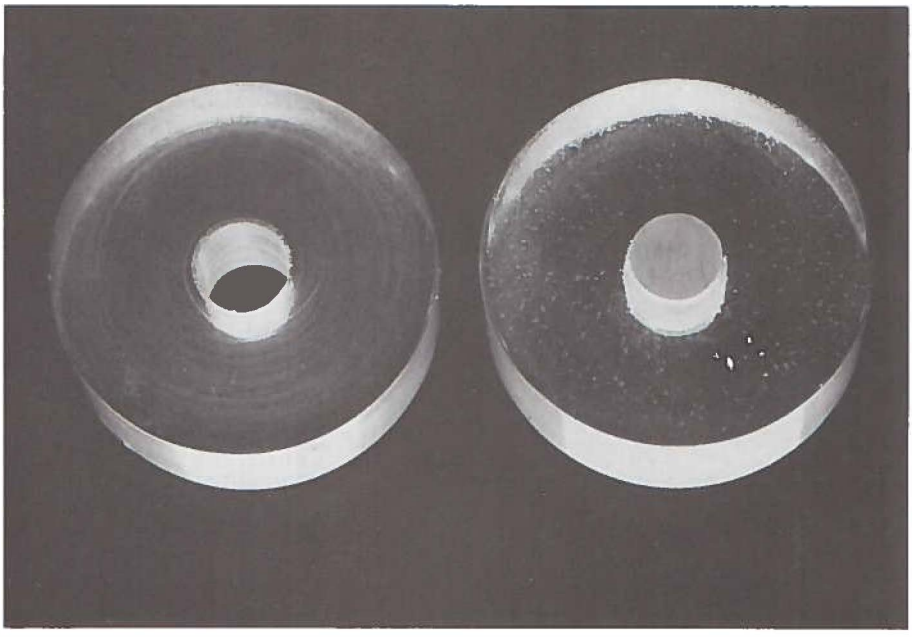

Figure 3.2
Sample holder-empty (left) and filled (right).

3.2.3.2. IN VIVO EXPERIMENT

To simulate the clinical situation as realistic as possible the cements were positioned in enamel. Freshly extracted bovine incisors were buccally flattened and polished, using waterproof sandpaper (400/600 mesh) and diamond lapping compound (6 µm) (see Figure 3.3 and 3.4).

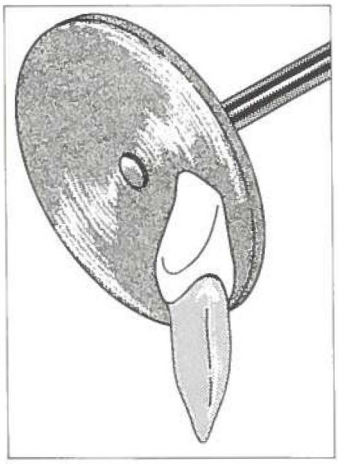

Figure 3.3
The buccal surface is flattened and polished.

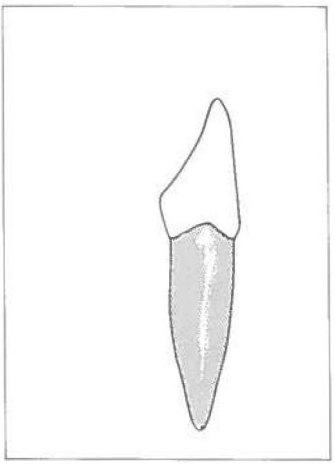

Figure 3.4
A flat area is created.

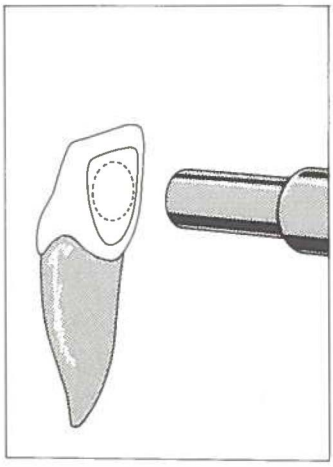

Figure 3.5
A small circular section is removed with a hollow drill.

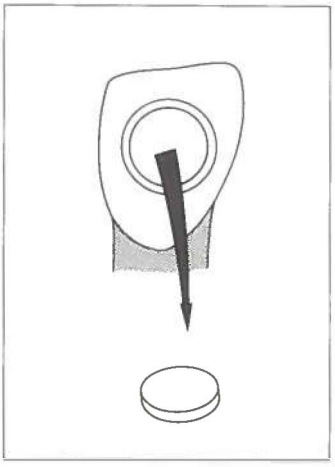

Figure 3.6
The final specimen is 3 mm thick and 10 mm in diameter.

The incisor was attached to a drilling platform with plasticine and with the use of a diamond coated hollow burr* (outside diameter 12 mm/inside diameter 10 mm) a small selected circular section was cut out of the incisor (see Figure 3.3 through 3.6).

The enamel surface was fixed to the tip of a non-rotating outside micrometer** with double-side adhesive tape. A teflon ring (inside diameter 11 mm/height 12 mm) was placed underneath the enamel specimen on a micrnscope glass slide (see Figure 3.7). Self curing acrylic repair material*** was mixed and poured into the teflon ring. Subsequently the circular enamel specimen was lowered and embedded parallel to the glass slide.

*Diamant Boart B.V. - Vianen/The Netherlands.

**Mitutoyo Mfg. Co., Ltd/Japan.

***Rapid Repair^{R} - De Trey/England.

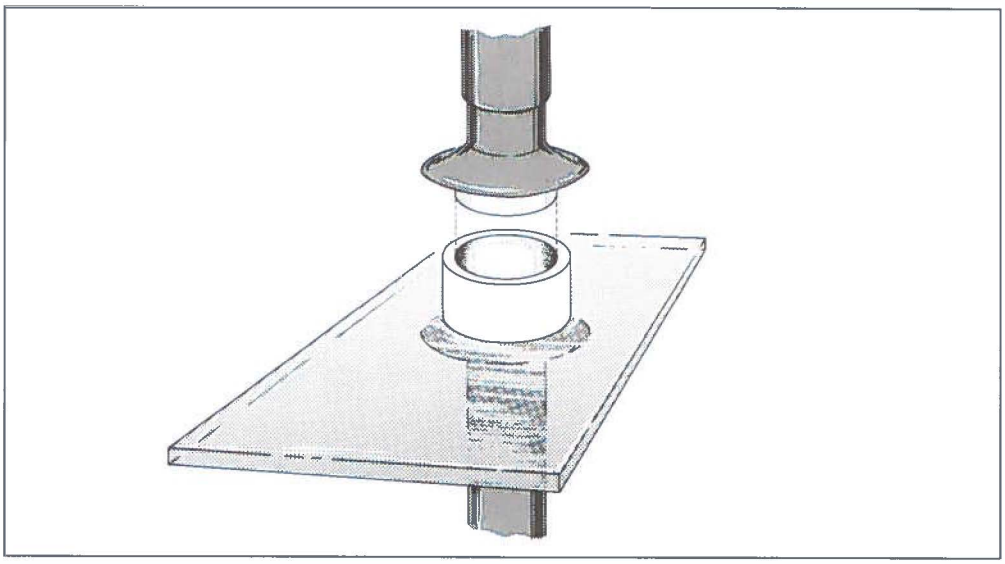

Figure 3.7

The enamel specimen -fixed to the upper-tip of the micrometer- can be lowered into a teflon ring, parallel to the glass slide.

Six cylindrical holes were subsequently drilled perpendicular to the surface (diameter 1.3 mm/depth 2 mm) -the centres being spaced exactly 2 mm- with a carbide tipped twist drill using a toolmakers bench. The six holes were placed as indicated in Figure 3.8; the asymmetry of the pattern makes individual holes easily recognizable. Subsequently, the acrylic underneath was ground away, as well as a layer of dentine, to make the slice as thin as possible ($\pm$ 3 mm). The outline was made as small as possible ($\pm$ 6 x 9 mm).

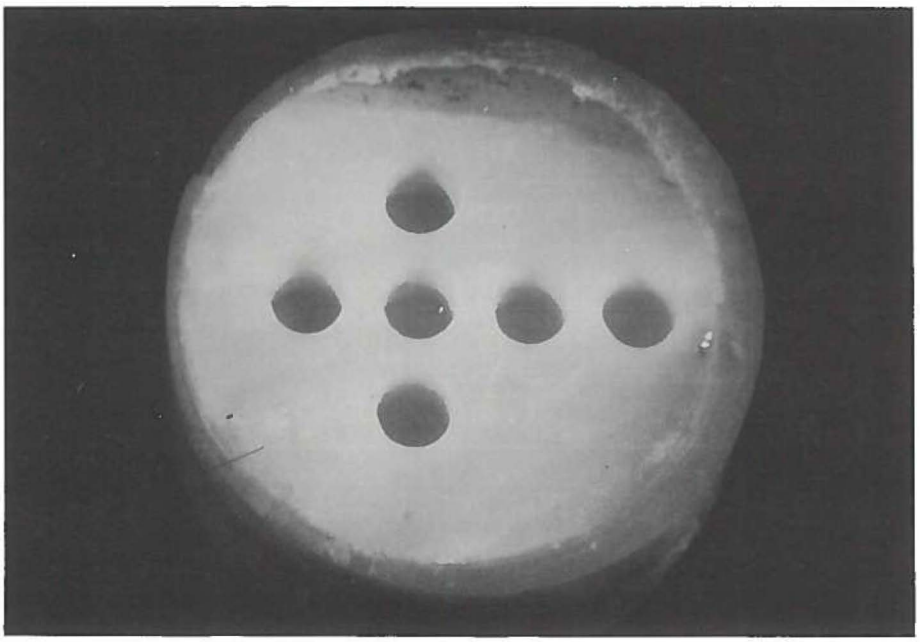

Figure 3.8
Six cylindrical holes drilled asymmetrically in an enamel slice.

A symbol was engraved in the surface next to the holes for coding. The six holes were finally filled, **each** with a **different** cement (see Figure 3.9) but always in the same sequence.

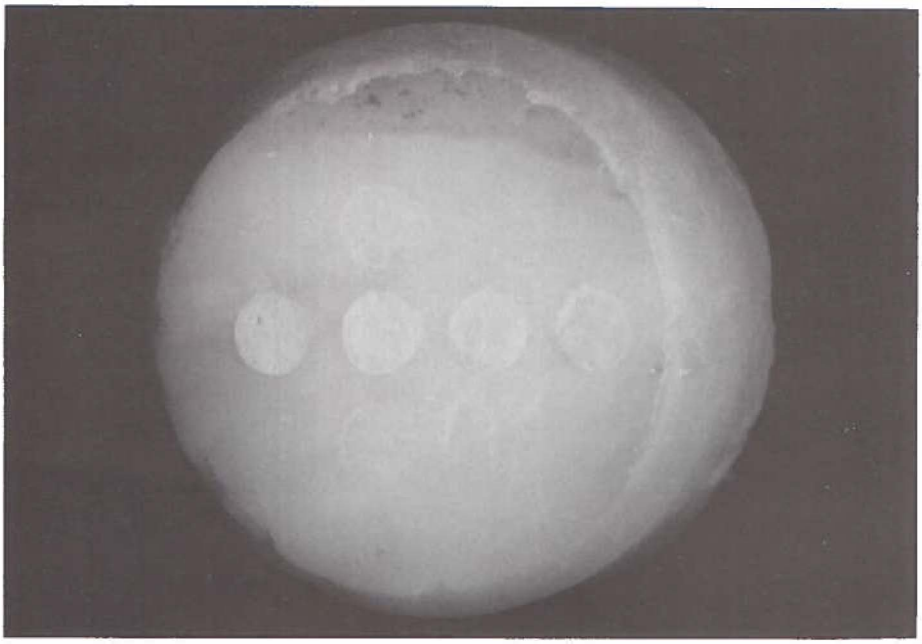

Figure 3.9
The same specimen as in Figure 3.8,
the holes are cement filled.

3.3. EXPERIMENTAL METHODS

3.3.1. IN VITRO EXPERIMENT

An apparatus as shown in Figure 3.10 was designed and built to create a forced flow of liquid perpendicular to the sample surface, simulating cement erosion and dissolution (Smink and Arends, 1980; Beech and Bandyopadhyay, 1983).

This was done by means of ten small nozzles (inner diameter 1 mm) which sprayed the test liquid over ten samples, mounted exactly underneath (see Figure 3.11, "e")

In the bottom of the same apparatus underneath the erosion samples -and thus using the same test liquid- a constant flow was created by the fluid coming through the nozzles and by the overflow "o" (see Figure 3.11, "f"). Ten samples of the same cement could be placed there. This set-up was connected to a closed circuit containing 11 liters test fluid. The liquid was constan-

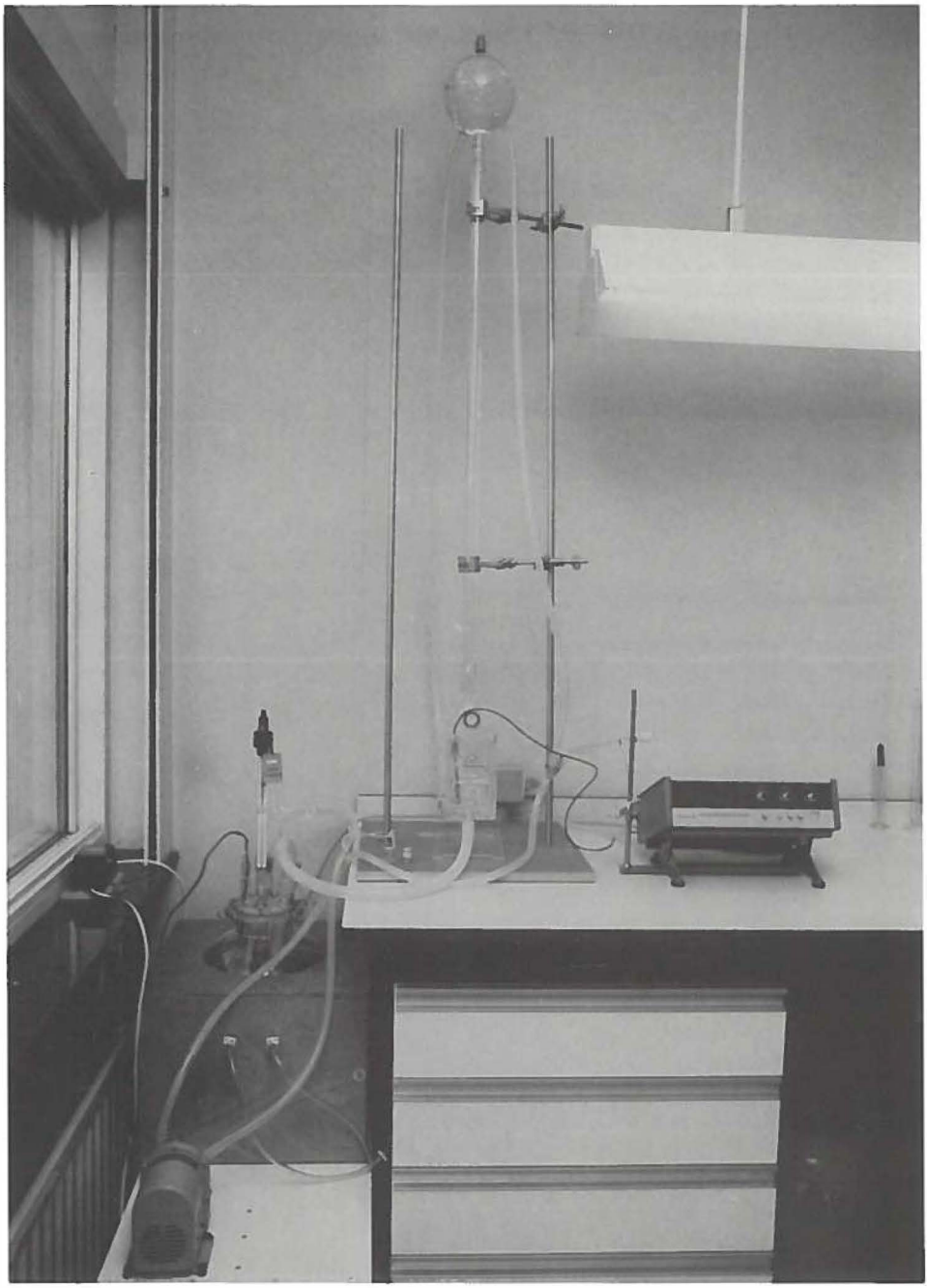

Figure 3.10

Experimental in vitro cement solubility test set-up.

Figure 3.11

Schematic representation of in vitro cement solubility test set-up.

o - overflow
n - nozzles
e - erosion samples
f - flow samples
p - pump
r - reservoir.

tly circulated using a pump*. The flow rate through each nozzle was 9 $l.h^{-1}$. The whole circuit was kept at 37°C by a immersion heater**, relay-connected to a contact thermometer***. The pH meter**** had been calibrated at 37°C. Temperature and pH were checked in the apparatus every 24 hours. The experiments always started using demineralised water as the test liquid for one week; the pH being 6. Subsequently, lactic acid was added in such amounts that the pH went down 0.5 a pH unit every time lactic acid was added.

5 to 7 days were used between pH steps, depending on wether the cement showed a strong reaction. Sample thickness measurements were done every 24 hours, as well as temperature and pH controls. Sometimes acid addition was necessary, especially in the range above pH 4, when the pH tended to rise very slowly during 24 hours: about 0.3 - 0.5 pH unit. Problems were the growth of algae in the circuit and loose particles obstructing the nozzles. These problems started after about a month, in spite of a small quantity of natrium-azide added to the test liquid.

3.3.2. IN VIVO EXPERIMENT

3.3.2.1. PATIENT SELECTION

All patients recently treated for full dentures at the Groningen dental school were screened.

Firstly, the participants had to live within reasonable proximity from the school because of the repeated appointments.

Secondly, their dentures had to be of sufficient thickness to accommodate the samples; the most suitable location for this purpose -also the least irritating- is the buccal flange of the lower denture.

*Eheim model 581/Western Germany.
**Rena 100 W.
***Frowi FW 21/Western Germany.
****PHM 84 Radiometer/Denmark.

Thirdly, the patients had to wear their dentures **day and night**. If the lower dentures, containing the samples, were taken out of the mouth during the night, standardization is impossible. And last but absolutely not least:

The participants had to be willing to cooperate in the experiments.

From a group of about 275 persons, 85 lived within the city limits and received a questionnaire; 46 responded. 28 were invited for a denture inspection. An explanation of the experiment and its consequences was given. Finally 21 were selected. Ultimately 10 subjects wore the cement samples for the measurements of material loss; 6 others did wear identical samples for infrared spectroscopy. The first group consisted of 6 men (aged 50 to 62 years, mean 56 $\pm$ 5) and 4 women (aged 45 to 60 years, mean 52 $\pm$ 7). The second group consisted of 5 women (aged 44 to 62 years, mean 52 $\pm$ 8) and one man (63 years).

3.3.2.2. POSITIONING OF THE CEMENT SAMPLES IN THE DENTURES

To ensure reproducibility it was necessary to reposition the specimen, and therefore the denture, exactly during specimen replication. The method used was partly as described previously by Gelhard (1982). Firstly, the denture was oriented in such a way that the buccal flange (in which the specimen was to be placed) was positioned as horizontally as possible. This was done by placing the denture on an aluminium U-shaped block with the aid of plaster (see Figure 3.12). In the buccal flange of the lower denture a hole, somewhat larger then the specimen, was fraised as well on the left as on the right side. Secondly a more accurate horizontal positioning of the specimen itself was done with the aid of a vertical non-rotating micrometer system as shown in Figure 3.13. The specimen was fixed to the tip of the micrometer with double sided adhesive tape and a small amount of liquid cold curing resin was poured into the hole. The tip of the micrometer was lowered until the specimen was level with the buccal flange. The micrometer was kept in position until resin setting; after-

wards small irregularities and defects were corrected. Figure 3.14 shows the specimens in place in the denture.

The set-up of Figure 3.13 made it possible to reposition the cement holders' surfaces perfectly horizontally during the successive replica-takings. A set (left and right) of individually custom-made plaster casts for each patient, as shown in Figure 3.12, was stored for future use.

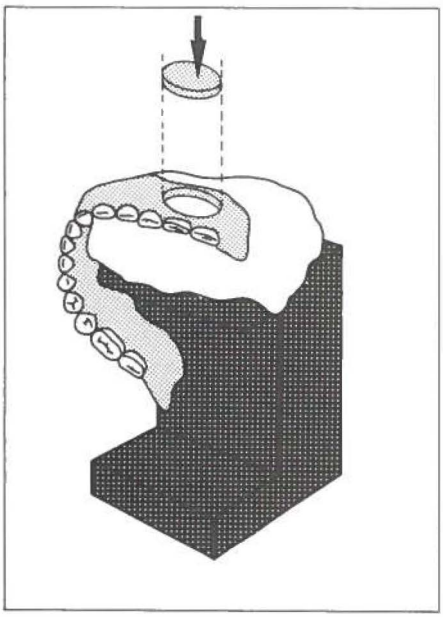

Figure 3.12
Space is created to enable positioning of cement sample holder.

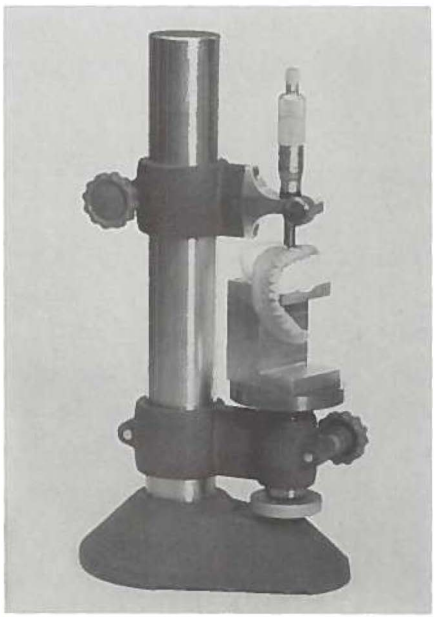

Figure 3.13
Horizontal positioning of the cement sample holder by means of a vertical non-rotating micrometer.

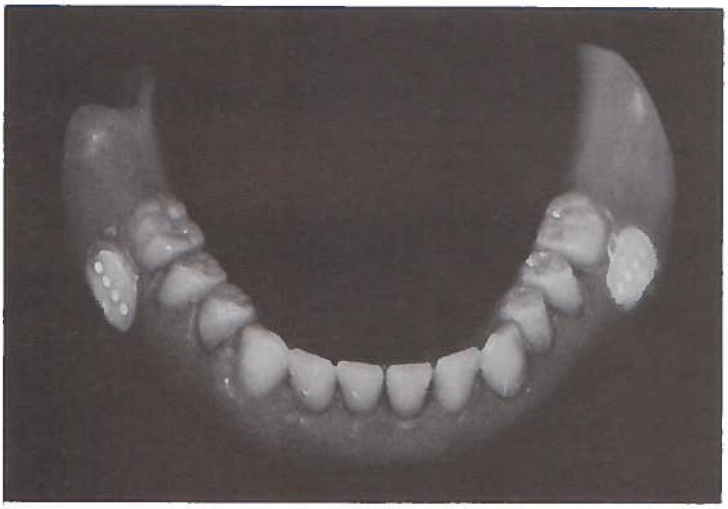

Figure 3.14
Enamel slices containing cement samples fixed in lower denture.

3.3.2.3. IN VIVO EXPERIMENT

After cement insertion in the dentures as described in Chapter 3.3.2.2., the patients were instructed to wear them day and night; a written note had to be made when an exception to this regime took place. Furthermore they should clean their dentures as usual, meaning that a brush could be used with water, soap or a toothpaste, but to refrain from any chemical cleansing agent during the experiment.

Firstly, baseline replicas were made of the cement surfaces, using a light-bodied silicone impression material*, before the specimens were placed in the mouth. Secondly, replicas of the same surfaces were made again after 1, 2, 3, 5, 8, 12 and 24 weeks; 50% of the samples were followed up to 48 weeks.

The replicas were made in the following way. The lower denture was repositioned in the custom made plaster mold in the original set-up (see Chapter 3.3.2.2). With some occlusal indicator wax** on the outside a teflon ring (inner diameter 11 mm/height 3

*President^{R} light bodied - Coltène/Switzerland.
**Occlusal indicator wax^{R} - Kerr U.S.A.

mm) was placed over and a little above the specimen (see Figure 3.15). Light-bodied impression material was mixed, inserted over the specimen surface in a thin layer initially and blown into all details with a soft air stream. Then more material was added and topped with a small glass slide (± 20 x 25 mm). The micrometer was then lowered so that its tip was in complete contact with the slide, which in its turn was in touch with the teflon ring (see Figure 3.16). In this way it was ensured that the bottom of the replica -and therefore its surface- was absolutely parallel when photographed later on under the scanning electron microscope with each replica and every time again.

Finally the replicas were trimmed, cleaned ultrasonically and fixed with an adhesive* to a small aluminium stub (diameter 13 mm) for future manipulation (see Figure 3.17).

*President^{R} adhesive - Coltène/Switzerland.

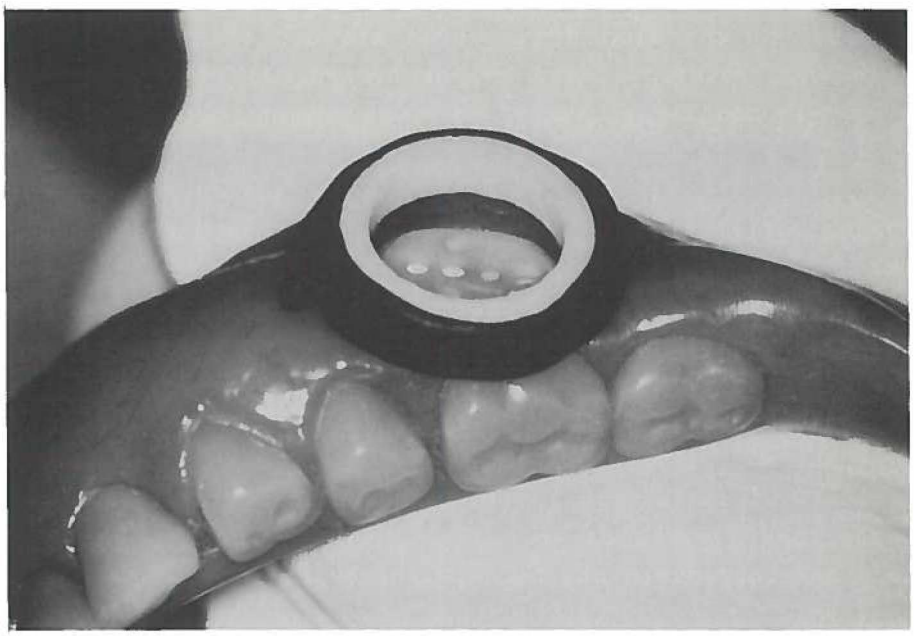

Figure 3.15
Teflon ring mounted over cement samples.

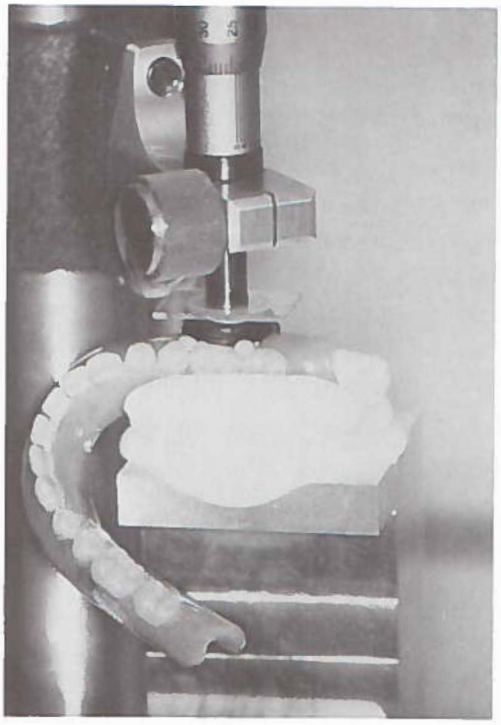

Figure 3.16
Micrometer lowered over cement samples
in position and impression material applied.

Figure 3.17
Replica from sample "S" taken after 5 weeks.

3.4. MEASUREMENTS

3.4.1. IN VITRO EXPERIMENT

The thickness loss of the cement samples was determined with a micrometer system (see Figure 3.18) and this loss was taken as a measure of the dissolution of the material. Each sample was placed underneath the measuring device*; a notch ensured an exact repositioning every time (see Figure 3.19).

Then the measuring tip was lowered and the thickness of the sample determined with an accuracy of 0.01 mm.

*Dial Gage stand model DGS-M - Mitutoyo Mfg. Co Ltd/Japan.

Figure 3.18
Cement sample under dial gage micrometer,
thickness being between 5.12 and 5.13 mm.

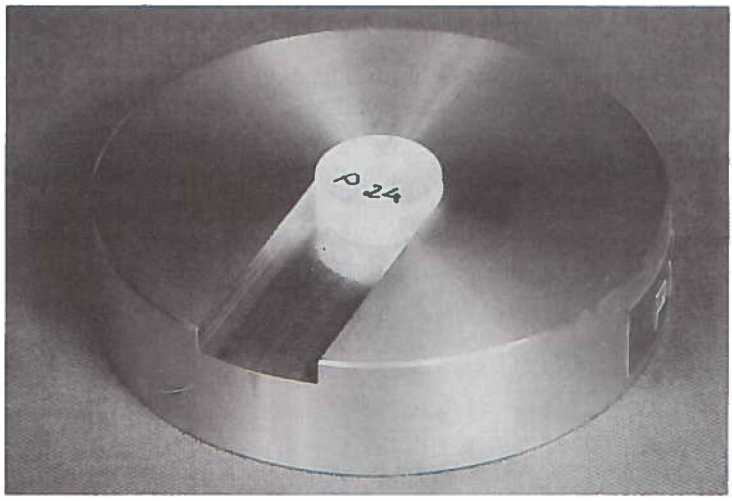

Figure 3.19
Cement sample in guiding notch for exact repositioning.

3.4.2. IN VIVO EXPERIMENT

Replicas:

All replicas of the cement surfaces, as described in chapter 3.3.2.3, were gold-plated (10 nm thickness) using a Balzers sputtering apparatus (type 07/120B)**.

S.E.M. measurements:

Stereo pictures were made of the replica using a Jeol-35C Scanning Electron Microscope**; the enlargement was 50x. Tilts of plus and minus 3 degrees with respect to the horizontal position were employed for the two stereographs. These stereoscopic pairs of photographs were evaluated at a Hilger and Watts Stereometer*** SB 180 (see Figure 3.20) and the depth "d" (see Figure 3.21), being the distance between the cement surface and the original enamel surface, calculated.

*Balzers UNION - Balzers/Liechtenstein.
**Japan Electron Optics Laboratory Co, Ltd-Tokyo/Japan.
***Rank Precision Industries Ltd. - Leicester/England.

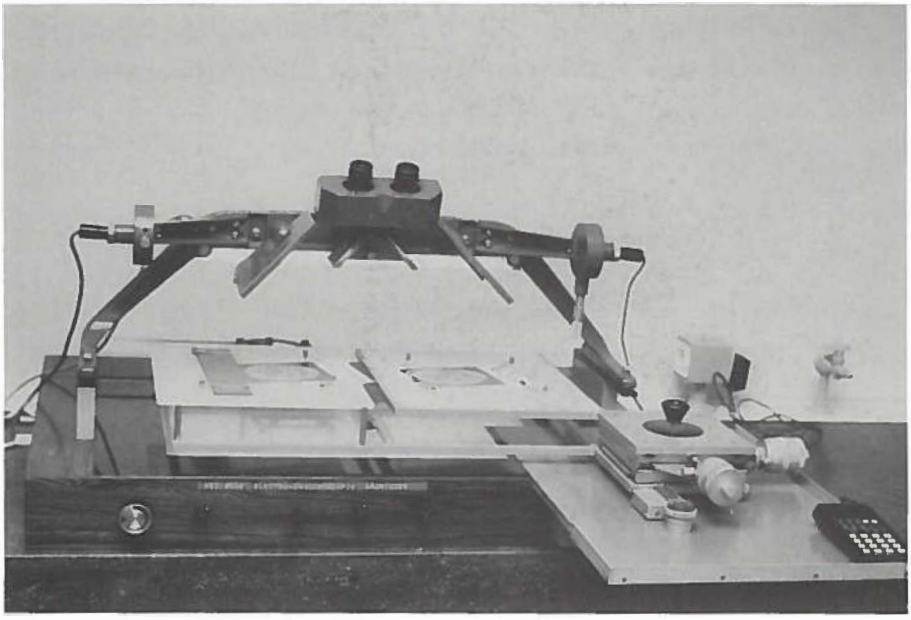

Figure 3.20

Hilger and Watts Stereometer with a stereoscopic pair of photographs.

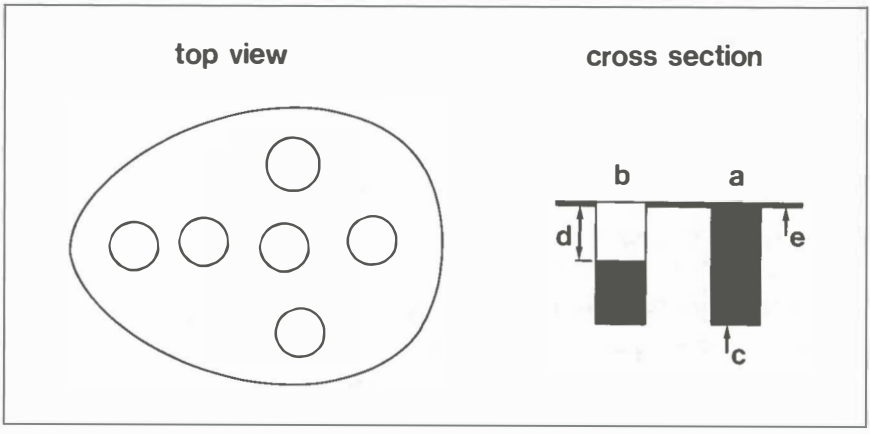

Figure 3.21

Schematic representation of sample:

a - cement filled hole

b - cement partly dissolved

c - cement

d - distance measured

e - enamel surface.

Therefore the coordinates of four points on the edge of each hole -containing cement- were determined. Then the same was done for the corresponding points on the cement surface plus the co-ordinates of the centre (see Figure 3.22).

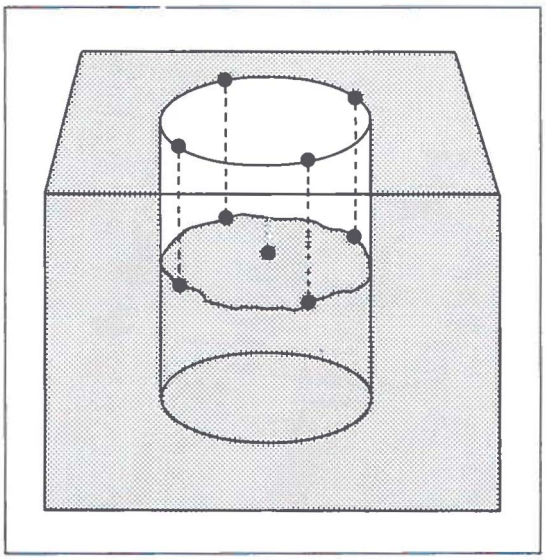

Figure 3.22
Schematic representation of a cement - containing hole with measuring points.

From these values the mean distance between the enamel surface and the cement surface could be calculated.

Depth "d" (see for details Jongebloed, 1976) can be calculated from the formula

$$d = \frac{1}{M}\left(\frac{\Delta X}{\sin\alpha} + X_r \operatorname{tg} 0.5\ \alpha\right)$$

Here, M is the magnification, α is the total tilt angle (here 6^{o}), ΔX and X_r are parameters directly obtained from the Hilger and Watts Stereometer.

3.4.3. ACCURACY AND REPRODUCIBILITY

The parameters in the formula of "d" have been discussed in detail by Jongebloed (1976) and a theoretical accuracy of 2-5%, depending on the magnification, may be expected.

To test the accuracy of the replica technique a separate experiment was carried out with tiny holes drilled in a flat piece of polished brass. This material was used because the surface is smooth and replicas can be removed easily.

Figure 3.23 shows three typical holes at low magnification (16x) under the S.E.M. Some scratches present in the polished surface are observable.

Figure 3.24 shows a small segment of the inner part of a hole at 150x magnification. The scratches on the surface, being a few micrometers in diameter, are clearly observable as well as the drill marks.

In Figure 3.25 the same specimen is presented, but now as a replica.

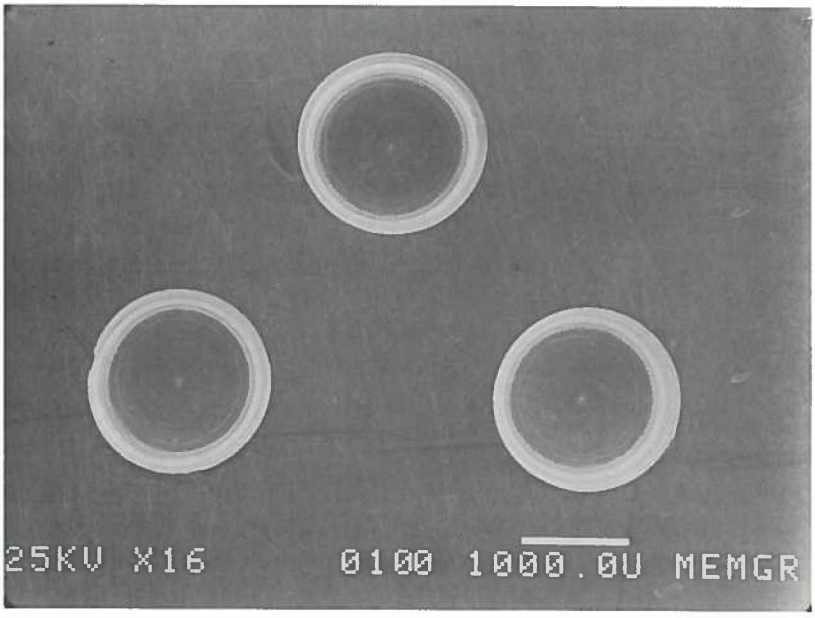

Figure 3.23
SEM micrograph of brass holes.

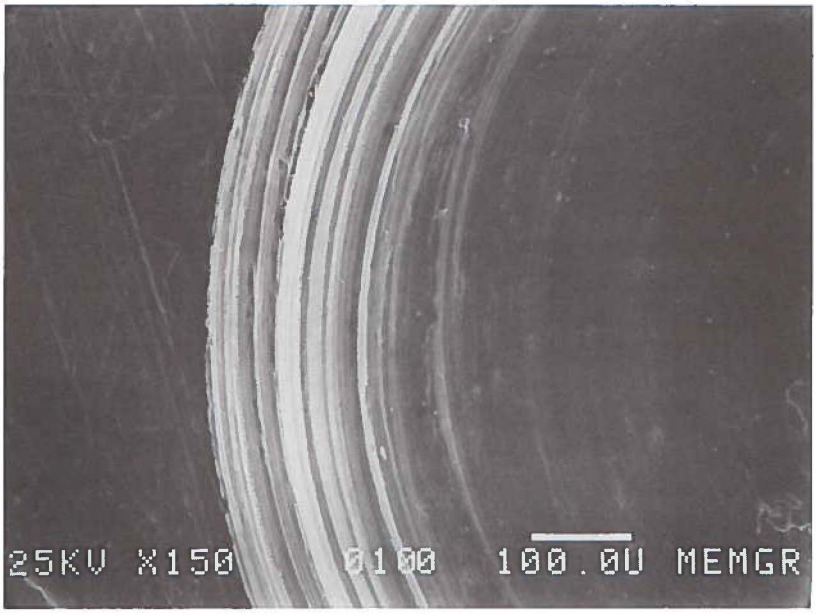

Figure 3.24
Section of brass hole.

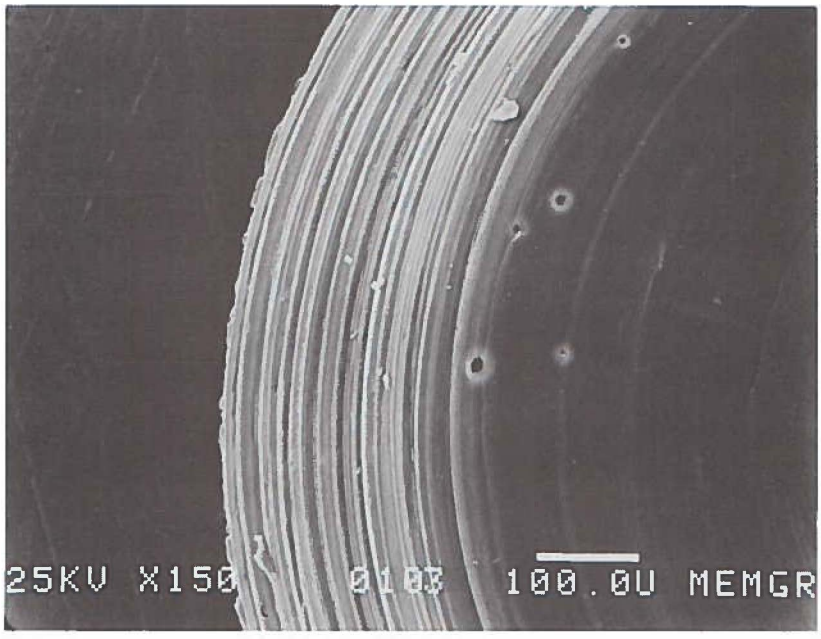

Figure 3.25
Replica of the section in Figure 3.24.

To test the reproducibility, measurements were carried out on some cement specimens **directly** as well as on several replicas.

The reproducibility is in the order of 7 - 10 μm (repeated measurements, see Table 3.II).

Table 3.II Repeated measurements on a cement specimen; the hole depth is presented.

measurement nr.	original specimen	replica
1	120	120
2	118	120
3	117	107
4	120	102
5	102	109
6	107	105
average depth ± SD	114 ± 7	110 ± 7

Because in this case always distance **differences** were measured, the total error is estimated to be in the order of 15 μm.

The reproducibility is partly determined by instrumental errors but especially by the cement surface irregularities (see Figures 3.26 and 3.27. Table 3.II shows also that the errors induced by the replica technique itself are **smaller** than the total error mentioned above.

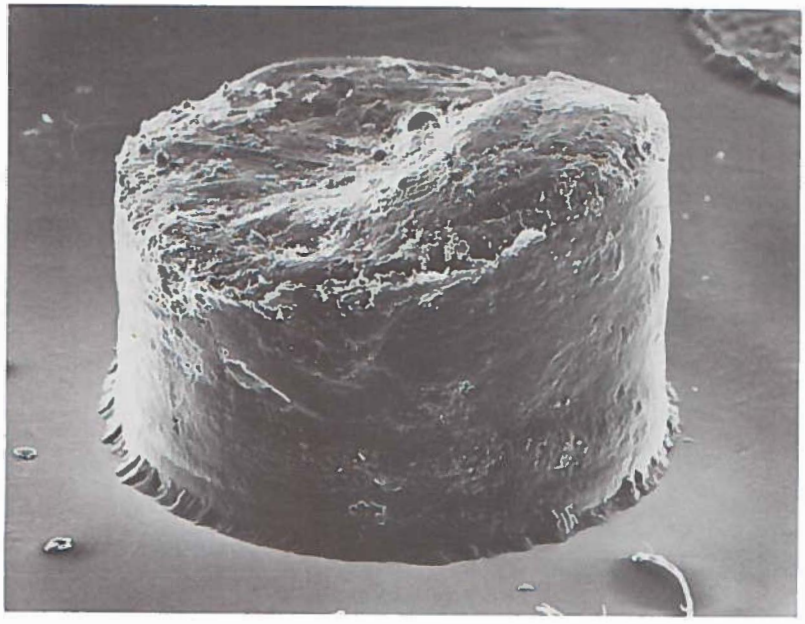

Figure 3.26

Replica of the cement surface (50x) after 24 weeks.

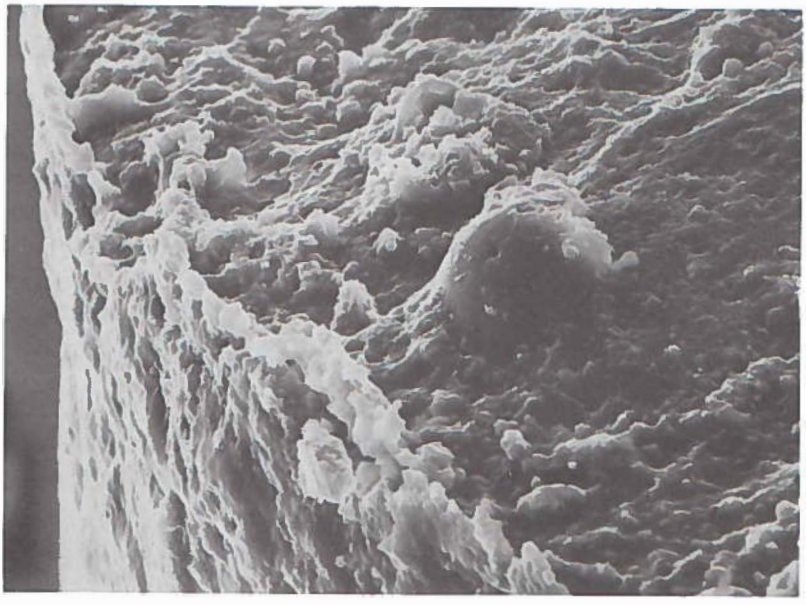

Figure 3.27

Enlarged detail of the same specimen (500x).

3.5. OTHER METHODS

3.5.1. INFRA-RED SPECTROSCOPY

Samples of the six luting cements as tested in the previous experiments were mixed and put into sample holders, consisting of a perspex strip (3 x 3 x 12 mm) in which six holes (1.3 mm diameter, 2 mm deep) were drilled (see Figure 3.28).

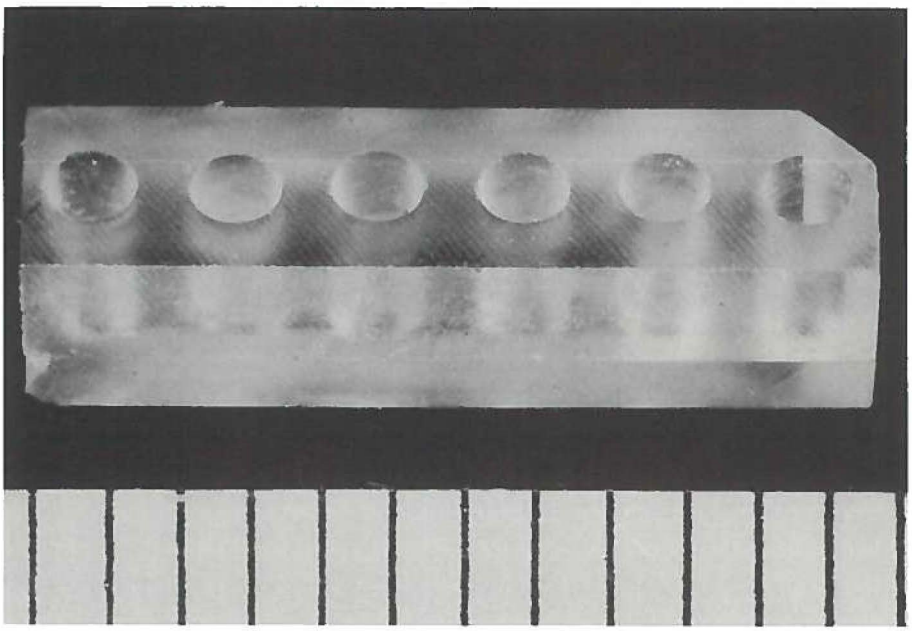

Figure 3.28
Perspex sample holder for infra-red spectroscopy;
the scale underneath denotes millimeters.

From the earlier collected group of patients six test persons, not participating in the in vivo experiment, were selected.

The sample holders were mounted in the patients' lower dentures, one at the left and one at the right hand side, buccally in the first molar region exactly as in the other in vivo experiment (see Figure 3.29). After the same intervals as mentioned: after 1, 2, 3, 5, 8 and 12 weeks, the two sample holders were taken out from a denture and stored in 100% humidity before being submitted to infra-red spectroscopy.

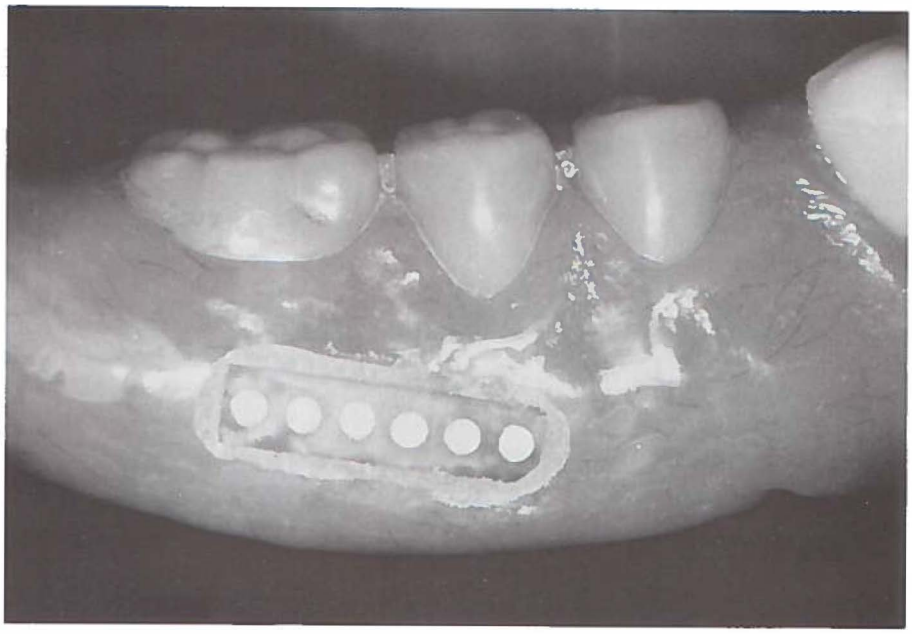

Figure 3.29
Perspex sample holder in situ.

3.5.2. SCANNING ELECTRON MICROSCOPY

Scanning electron microscopic pictures were made for surface visualization. First of all, S.E.M. micrographs were made of the freshly drilled holes in an enamel slice, before being filled with cement, sectioned through the holes. The edge as well as a deeper area were photographed. Then a cement-filled sample, not worn by a patient, was again sectioned through the holes and pictured, the cement surface as well as the edge. Subsequently the cement was taken out and the edge and inner surface of the hole was pictured again. Finally the same was done with a sample, worn for 24 weeks in vivo.

3.6. SALIVA

To determine possible correlations between extent and/or rate of the cement disintegration and salivary properties, samples of whole unstimulated saliva were taken from all 10 participants in this experiment and the following parameters determined:

1. Preliminary pH indication in the mouth.
2. pH of whole saliva.
3. Salivary buffercapacity.

3.6.1. SALIVA COLLECTION

The patients were asked not to eat, drink or clean their mouth and dentures for one hour before saliva collection.

The patients were instructed to spit whole saliva in a small plastic container, that was closed immediately; salivary flow rate was not stimulated.

When 5 ml saliva was collected, pH and buffercapacity were determined immediately. The average collection time of the sample was about 10 minutes; in one case only the collection had to be stopped after 15 minutes.

3.6.2. PRELIMINARY pH MEASUREMENT

Directly on arrival and before saliva collection, a preliminary pH measurement was done directly in the patients' mouth by means of special indicator paper* pH 6.4-8.0 and pH 5.4-7.0.

3.6.3. LABORATORY pH DETERMINATION

The pH was measured with a Radiometer (PHM 64 research pH-meter) in 1 ml saliva in a **closed** polyethylene bottle. The accuracy was estimated to be 0.05 pH unit.

*E. Merck - Darmstadt/Western Germany.

The mini-electrode employed was a 6 mm diameter Radiometer (GK 23210 combined glass calomel). The pH value of each patient was determined in duplo.

3.6.4. BUFFERCAPACITY DETERMINATION

The salivary buffercapacity was estimated by adding slowly a 0.020 Mol lactic acid solution (pH = 2.8) to 1 ml saliva by means of an automatic Radiometer burette (automatic burette ABU 13 T.T.T. 60 titrator). The lactic acid addition speed was 0.55 $ml.-min^{-1}$.

During acid addition the solution was slowly stirred magnetically. The maximum amount of lactic acid added was 1.5 ml. Every second the pH and amount of lactic acid added were registrated and printed on a Hewlett Packard 5150A printer. The salivary buffercapacity will be expressed as: the amount of 0.020 Mol lactic acid needed to bring the pH of 1 ml saliva to pH = 6.0, 5.0 or 4.5, respectively.

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CHAPTER FOUR

IN VIVO CEMENT SOLUBILITY RESULTS

4.1. INTRODUCTION

In this chapter the results of the **in vivo** experiment will be presented and compared with other in vivo research results from the available literature.

4.2. MATERIALS AND METHODS

The test group consisted of 10 participants. Each patient had two enamel slices (used as cement sample holders) in the lower denture: one on the left and one on the right hand side of the mouth. Each slice had six holes; each hole was filled with a different cement, but always in the same sequence. In this way 20 samples of each cement could be tested simultaneously.

The cements tested were:

Zinc phosphate cements	Standaard	(referred to as Z1)
	Phosphacap	(referred to as Z2)
Polycarboxylate cements	Durelon	(referred to as P1)
	Bondalcap-C	(referred to as P2)
Glass ionomer cements	Chem Bond	(referred to as G1)
	Fuji I	(referred to as G2)

Material loss was measured quantitatively after 1, 2, 3, 5, 8, 12, 24 and -in 50% of the test group- 48 weeks. Replicas were made and measured using Scanning Electron Microscopy and Stereometry as described already in Chapter 3.

At the end of the test period the slices with the remaining cement were carefully taken out from the dentures and stored in water.

The prostheses were repaired and returned to the original state.

4.3. RESULTS

4.3.1. INDIVIDUAL PATIENTS

4.3.1.1. PATIENT NR. 1

From Figure 4.1 it is obvious that both zinc phosphate cements (Z1 and Z2) dissolved at nearly the same rate.

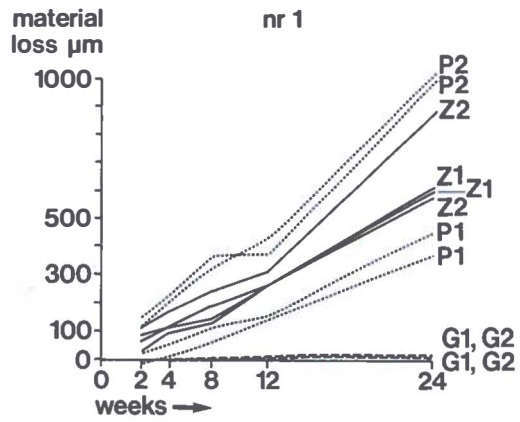

Figure 4.1

Cement dissolution as measured in the mouth of patient nr. 1.
Two identical characters denote the samples on the left and right hand side.

One polycarboxylate cement (P1) dissolved distinctly less than the zinc phosphate cements, the other polycarboxylate cement (P2) dissolved faster. The last point is difficult to understand, since these cements belong to the same type.

During the first three weeks some cements behaved irregularly; some tended so swell slightly in this period.

After three weeks however, the dissolution process for all cements is more or less linear with time.

The dissolution rate of the glass ionomer cements (G1 and G2) is so slow that it is hardly measurable, even after 24 weeks.

A different reaction between the left and right hand side of the mouth can be observed, but -with this patient- the results of the various types of cement do not overlap.

Dissolution rates for patient nr. 1 as measured over 24 weeks in $\mu m.week^{-1}$:

Z1	Z2	P1	P2	G1	G2
25	30	17	41	0.5	+1

4.3.1.2. PATIENT NR. 9

Compared to patient nr. 1 the speed of dissolution is enormous (see Figure 4.2.).

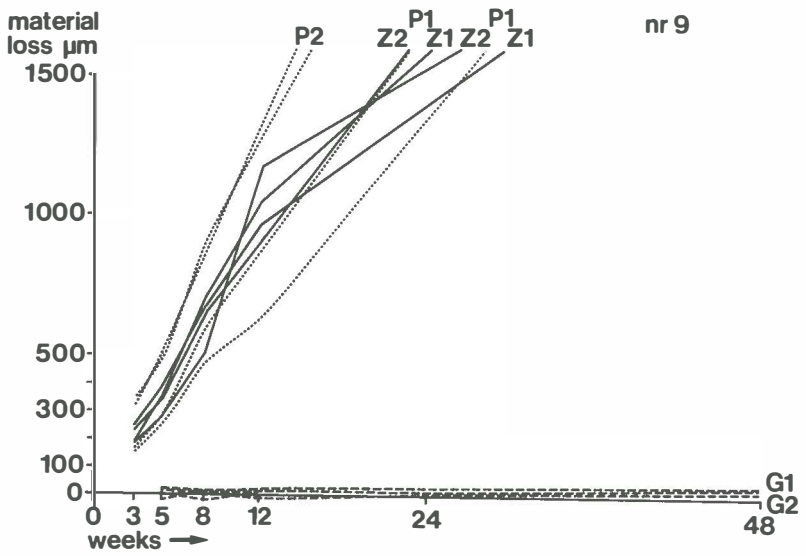

Figure 4.2

Cement dissolution as measured in the mouth of patient nr. 9.

Two identical characters denote the samples on the left and right hand side.

The zinc phosphate and the polycarboxylate cements had both completely disappeared from the holes long before the test period ended. Remarkable are the results of the glass ionomer cements. In conditions that for both other cement types were so destructive, the glass ionomer cements showed only a slight but negligible material loss. One polycarboxylate cement (P2) dissolves faster than the other cements, while the second polycarboxylate cement (P1) falls in the range of the zinc phosphate cements.

Dissolution rates for patient nr. 9 as measured in $\mu m.week^{-1}$:

cement / weeks	Z1	Z2	P1	P2	G1	G2
24	62	68	64	89	0.4	0.8
48	-	-	-	-	0.7	0.3

4.3.1.3. PATIENT NR. 10

Figure 4.3 shows the dissolution as measured in the patient with the **lowest** dissolution rate, demonstrating the wide range of possibilities between patients.

Both zinc phosphate and polycarboxylate cements are in the same range and partly overlap; one polycarboxylate cement (P2) is dissolved faster than the other (P1), but differences are minimal. One sample of the polycarboxylate cements even approached the glass ionomer cements' values, which again produced the best results.

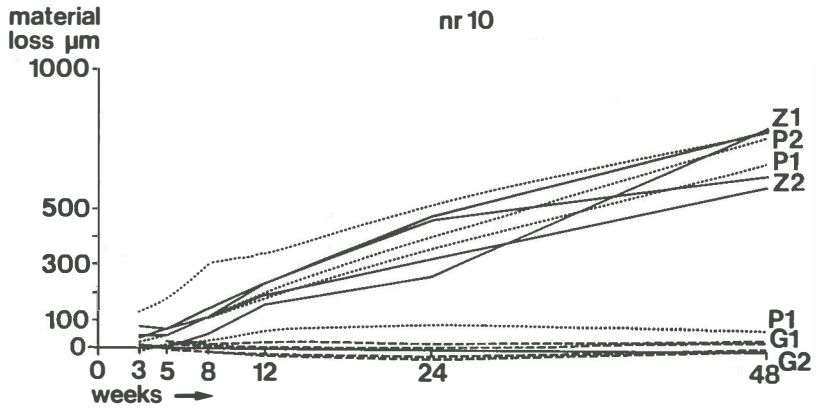

Figure 4.3

Cement dissolution as measured in the mouth of patient nr. 10.

Two identical characters denote the samples on the left and right hand side.

Table 4.I. Dissolution rates for patients nr. 1, 9 and 10 in µm.week^{-1}.

Patient nr.	Period in weeks	Cement Z1	Z2	P1	P2	G1	G2
1	24	25	30	17	41	0.5	+1
9	24	62	68	64	89	0.4	0.8
	48	-	-	-	-	0.7	0.3
10	24	15	16	9.5	19	0.5	+0.5
	48	16	12.5	8	16	0.8	0.3

4.3.2. AVERAGE RESULTS OF THE IN VIVO CEMENT SOLUBILITY

In Table 4.II and Figure 4.4 the average results for each cement are shown. It can be seen clearly that -after the first few weeks- the dissolution process becomes linear with time (t).

From Table 4.II the mean dissolution rate for each cement can be calculated, and this leads to values as shown in Table 4.IV.

Compared to the zinc phosphate cements, which do not differ very much, one polycarboxylate cement (P1) is somewhat more resistant while the other (P2) is distinctly more soluble. The glass ionomer cements consistently show superior dissolution characteristics compared to all other cement types.

Table 4.II. Cement loss (Δ) in µm. **Average** values for 20 samples between 0 and 24 weeks, and for 10 samples between 24 and 48 weeks. SD denotes the standard deviation in µm.

Cement			1	2	3	5	8	12	24	48 weeks
Standaard	(= Z1)	Δ	32	56	69	102	170	275	549	1.088
		SD	33	49	61	98	186	270	399	651
Phosphacap	(= Z2)	Δ	25	43	62	96	165	290	563	906
		SD	26	38	62	89	153	281	464	679
Durelon	(= P1)	Δ	21	29	31	60	115	194	410	890
		SD	30	39	53	82	152	266	422	723
Bondalcap-C	(= P2)	Δ	49	72	98	167	280	443	883	1.483
		SD	48	64	87	128	199	316	503	858
Chem Bond	(= G1)	Δ	-	-	-	13	14	20	24	26
		SD	-	-	-	33	34	34	38	27
Fuji-I	(= G2)	Δ	-	-	-	13	4	10	13	25
		SD	-	-	-	25	22	30	24	27

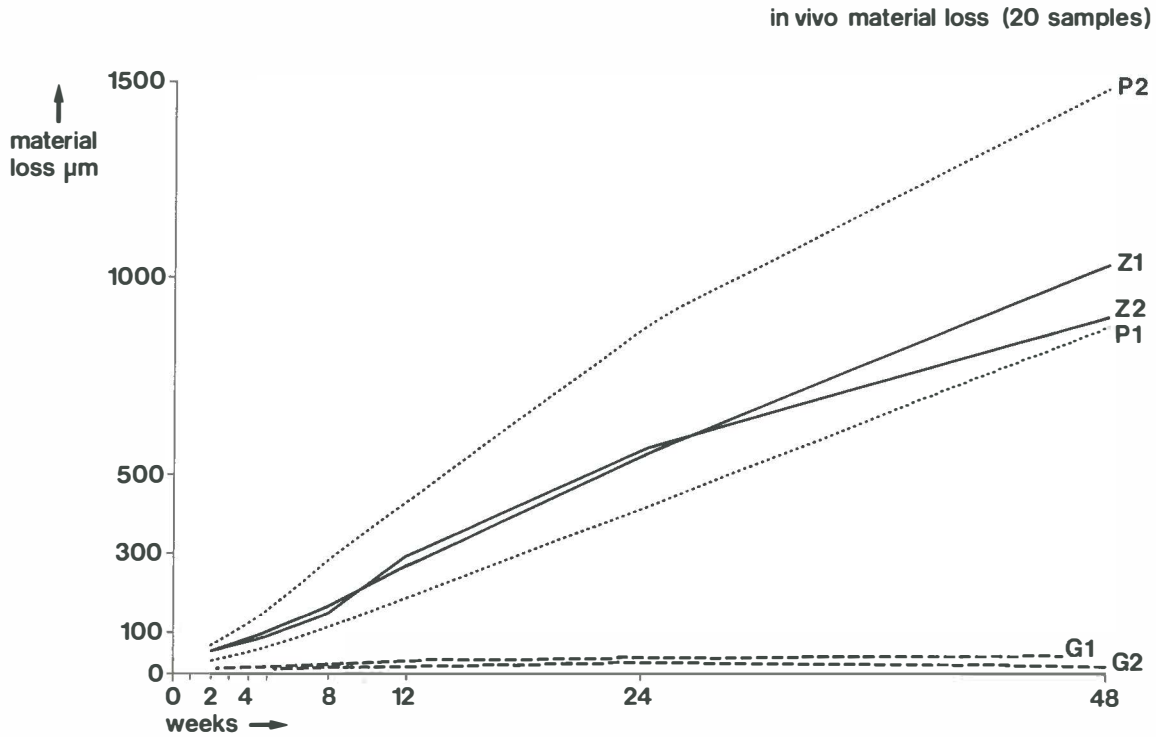

Figure 4.4

Mean cement dissolution values as measured for each cement.

There was a considerable variability between individual patients for the same cement. There are also differences between the right and left hand side of the same mouth.

From Table 4.III one can see that the variation in one patient can be up to a factor 2; see for instance participant nr. 6 (cement Z1).

To show the differences between left-right sides the data for the zinc phosphate and polycarboxylate cements are compiled in Table 4.III.

Table 4.III. Cement loss in µm after 24 weeks in vivo.

	LEFT				RIGHT			
Cement	Z1	Z2	P1	P2	Z1	Z2	P1	P2
Patient nr. 1	600	900	450	1.000	600	600	400	1.000
2	1.400	560	1.050	1.400	1.250	1.000	1.650	1.750
3	300	300	175	650	1.050	1.275	22	1.100
4	560	630	260	1.050	600	400	460	900
5	175	200	360	600	160	200	250	475
6	1.000	900	475	1.250	570	575	350	775
7	700	500	600	1.000	480	500	250	1.000
8	800	600	350	1.025	50	100	470	1.070
9	>2.000	>2.000	>2.000	>2.000	>2.000	>2.000	>2.000	>2.000
10	800	600	75	800	800	600	675	750
Mean values	833	720	635	1.075	834	794	722	1.080
± SD	± 535	± 501	± 570	± 406	± 540	± 552	± 643	± 460

Table 4.IV. Material loss for 6 cements during the whole test period in $\mu m.week^{-1}$.

Cement	8	12	24	48 weeks
Z1	21	22	22	22
Z2	20	24	23	18
P1	14	16	17	18
P2	35	36	36	30
G1	1.7	1.6	1.0	0.5
G2	0.5	0.8	0.5	0.5

The mean dissolution rate for the zinc phosphate cements, measured over the whole test period, amounts to 22 $\mu m.week^{-1}$ for cement Z1 and to 20 $\mu m.week^{-1}$ for cement Z2. Polycarboxylate cement P1 shows a dissolution rate of 18 $\mu m.week^{-1}$, while polycarboxylate cement P2 reaches over 30 $\mu m.week^{-1}$.

Finally glass ionomer cement G1 dissolves between 0.5 and 1.0 $\mu m.week^{-1}$ and glass ionomer cement G2 shows a constant value of 0.5 $\mu m.week^{-1}$.

4.4. THE IN VIVO CEMENT SOLUBILITY RATES: A COMPARISON WITH THE LITERATURE

The first clinical experiments were reported by Norman et al. (1969). After 30 days in an oral environment a loss of 2 - 4 $mg.cm^{-2}$ was measured for zinc phosphate cement. Great inter-patient variation was mentioned for the first time. It is not possible to compare these values with the data presented in this paper.

Osborne et al. (1978) found a loss of 127 µm for zinc phosphate cement and 50 µm for polycarboxylate cement after 24 weeks from holes 0.8 mm in diameter in crowns; large inter-patient differences were also noted.

Mitchem and Gronas (1978) studied cement solubility in vivo without mechanical erosion. After 6 months they measured a loss of 600 µm for zinc phosphate cement and 950 µm for polycarboxylate cement; comparable values in this study were 549 µm and 883 µm respectively.

For glass ionomer cement Mitchem and Gronas (1978) found a loss of 200 µm which could not be accounted for by mechanical erosion; this must be due to chemical and/or bacterial origin.

In 1983 Sidler and Strub studied cement positioned in holes in inlays, worn for about 14 months, and measured a loss of 500 µm for zinc phosphate cement. One glass ionomer cement (the same as G2 in our experiment) showed a loss of 100 µm while another brand lost 40 µm during the test period. Especially the last figures are in the same range as found in this investigation.

In the literature nobody had ever measured solubility in vivo longitudinally, **but always only at the start and the finish of an experiment.**

Mesu and Reedijk (1983) were the first to take measurements each month during a clinical test period of 6 months; unfortunately the material is not presented graphically.

Pluim et al. (1984[a,b]) showed in earlier studies for the first time that taking measurements longitudinally leads to the conclusion that the in vivo cement dissolution is linear with time.

The in vivo solubility **data**, published by several authors, have been calculated into solubility **rates** with the assumption that solubility in vivo is linear with time; the results are compiled in Table 4.V.

Table 4.V. Cement in vivo dissolution rates in $\mu m.week^{-1}$.

CEMENT	REFERENCE	RATE	REMARKS
zinc phosphate	this work	20 - 22	holes 1.3 mm
	Osborne et al., 1979	6	holes 0.8 mm
	Mitchem, 1978	23	holes 2.0 mm
	Sidler, 1983	8	holes 0.8 mm
polycarboxylate	this work	18 - 30	holes 1.3 mm
	Osborne et al., 1979	2	holes 0.8 mm
	Mitchem, 1978	36	holes 2.0 mm
glass ionomer	this work	0.5 - 1	holes 1.3 mm
	Mitchem, 1978	7	holes 2.0 mm
	Sidler, 1983	0.6 - 1.6	holes 0.8 mm

4.5. CONCLUSIONS

From the data presented, the following conclusions can be drawn:

1. The in vivo dissolution for all cements is **linear** with **time.**
2. All cements dissolve in vivo; even glass ionomer cements show some material loss.
3. There are considerable inter-patient variations, and also (although smaller) differences between the left and the right hand side of the same mouth.
4. The mean cement dissolution rates in vivo, measured in $\mu m.week^{-1}$ are: zinc phosphate 20 - 22.
   polycarboxylate 18 - 30.
   glass ionomer 0.5 - 1.

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CHAPTER FIVE

IN VITRO SOLUBILITY TESTS

5.1. INTRODUCTION

In this chapter the results of the erosion and flow solubility tests, carried out as described in chapter 3.3.1, are presented and compared with the available literature.

5.2. MATERIALS AND METHODS

Of each cement 10 samples, described in detail in chapter 3.2 were made. 5 Samples were submitted to the erosion test, while the other 5 were tested in the flow situation. As the apparatus could accommodate 10 samples for erosion as well as for flow, two different brands of the same type of cement could be tested simultaneously in a given test liquid.

The liquid circuit shown in Figure 3.10 was first filled with distilled water, circulated and brought up to 37^{o}C. Subsequently the samples were placed in position as in Figure 3.11. Every 24 hours the following measurements were carried out: material loss, pH and temperature.

In previous experiments using 10 identical samples of each cement for both test conditions (Pluim & Arends, 1981) it was shown that the standard deviation **between** specimens was very small and in the range of 1%. In these experiments 5 samples for each test condition are adequate.

5.3. RESULTS

5.3.1. ZINC PHOSPHATE CEMENTS

The data are compiled in Figure 5.1.

It was observed that, while the pH was gradually lowered from 6.0 to 5.0, a negligible material loss was noticed during the first 4 weeks.

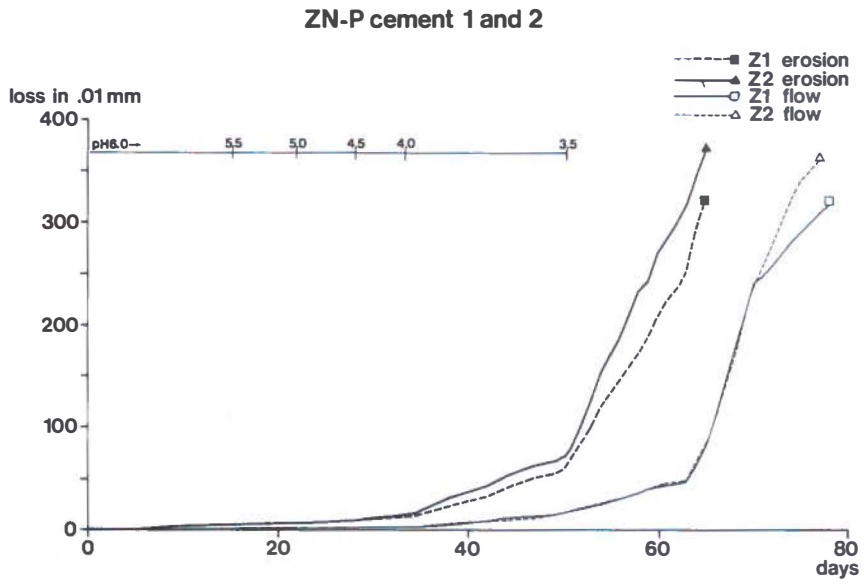

Figure 5.1

Erosion and flow dissolution for two zinc phosphate cements at 37°C.

However at the 28th day, the pH being 4.5, the erosion samples started to react slowly, the reaction became more pronounced when one week later the pH was lowered to 4.0. At this pH dissolution was continued for two weeks. During the same period the samples under flow conditions reacted in a similar way to the erosion samples at pH 4.5 (see Figure 5.1).

After 7 weeks (at pH 3.5) the dissolution rate went up very strongly for the erosion samples, while the flow samples again reacted as the erosion samples did at a pH 0.5 unit higher.

Finally, the erosion samples being dissolved nearly completely, at 63 days the pH was lowered to 3.0. The dissolution rate for the flow samples was nearly the same as for erosion at pH 3.5.

If we compare the sensitivities of the two tests -erosion versus flow- the flow test is less sensitive than the erosion experiment, the last one showing a more distinct difference between the two brands starting around the 35^{th} day at pH 4.0.

5.3.2. POLYCARBOXYLATE CEMENTS

At pH 5.5 and downwards until pH 4.5 a very slow reaction could be detected with cement P1, a reaction that could be seen in the erosion as well as in flow samples. Cement P2 showed no measurable material loss during these conditions.

A marked difference started after 10 days when the pH was lowered to 4.5. Cement P1 continued reacting at the same slow rate as before, while cement P2 started to erode more quickly as can be seen in Figure 5.2 in the 10-17 days period. This speed increased when a pH 4.0 was introduced and cement P2 disappeared in a few days from the erosion samples. In contrast cement P1 continued to erode at about the same rate as before. Only when pH 3.5 was reached, did the dissolution rate increase.

As far as the flow experiment is concerned the same phenomena were observed, but starting a 0.5 pH-value later. At pH 4.0 cement P2 dissolved about twice as fast as cement P1 and this ratio nearly tripled at pH 3.5.

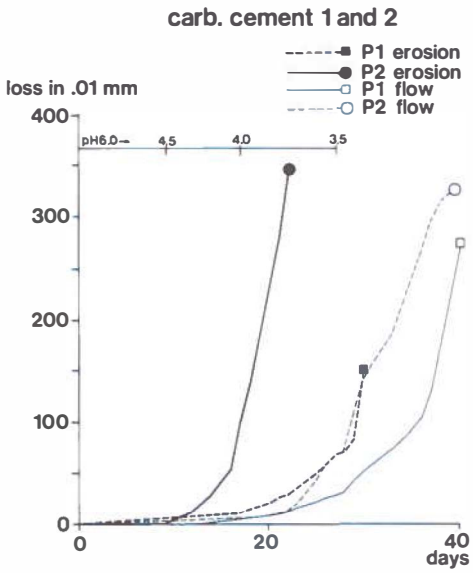

Figure 5.2.

Erosion and flow dissolution for two polycarboxylate cements at 37°C; the erosion experiment was stopped after 30 days.

5.3.3. GLASS IONOMER CEMENTS

This cement did not react, in erosion or flow tests, at all pH values above 3.0 (see Figure 5.3). Since this value is not reached under normal oral conditions, in vivo material loss of this type of cement can be contributed only to mechanical wear and/or direct bacterial action.

When the test conditions reached pH 3.0, both cements reacted, but differently. Cement G1 started to erode slowly, but about four times as fast as cement G2. Cement G1 dissolved in the flow test exactly as fast as cement G2 eroded, while cement G2 itself still showed nearly no reaction in the flow test.

As can be seen in Figure 5.3 these differences continued in the pH 2.5 range, where dissolution increased.

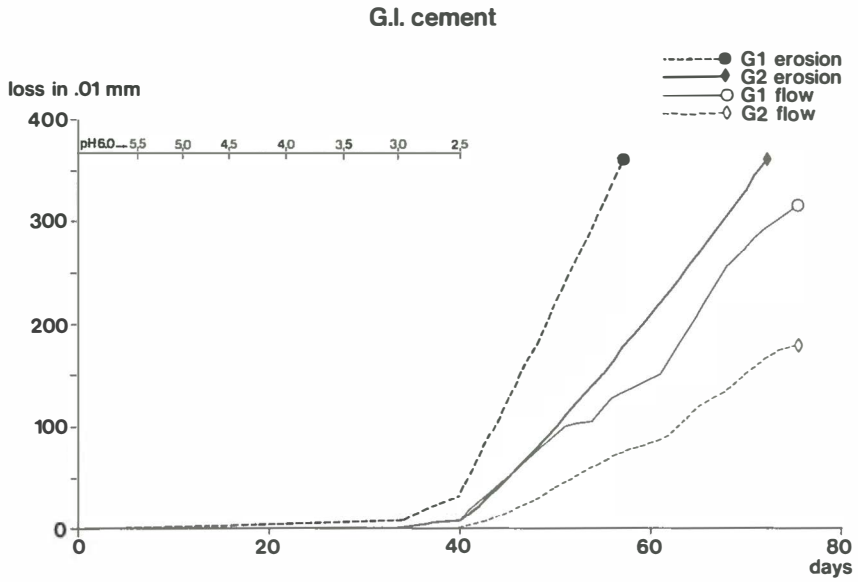

Figure 5.3.
Erosion and flow dissolution for the two glass ionomer cements at 37°C.

Finally all dissolution rates, erosion and flow, are recorded together in Table 5.I and Figure 5.4 (see next pages).

Table 5.I. Erosion and flow dissolution rates in $\mu m.day^{-1}$ at 37^{o} for all 6 cements.

Zinc phosphate cement Z1: Standaard
Z2: Phosphacap
Polycarboxylate cement P1: Durelon
P2: Bondalcap-C
Glass ionomer cement G1: Chem Bond
G2: Fuji I.

Lactic acid	EROSION						FLOW					
pH	Z1	Z2	P1	P2	G1	G2	Z1	Z2	P1	P2	G1	G2
6.0	3	2	10	0	0	0	0	0	6	3	0	0
5.5	3	1	3	0	0	0	1	0	3	0	0	0
5.0	3	4	3	0	0	0	0	1	0	0	0	0
4.5	10	14	14	183	0	0	1	1	3	5	0	0
4.0	30	37	57	533	0	0	8	8	27	71	0	0
3.5	138	176	230		0	0	23	23	67	187	0	0
3.0					34	11	186	222	246	225	11	0
2.5					192	109					89	52

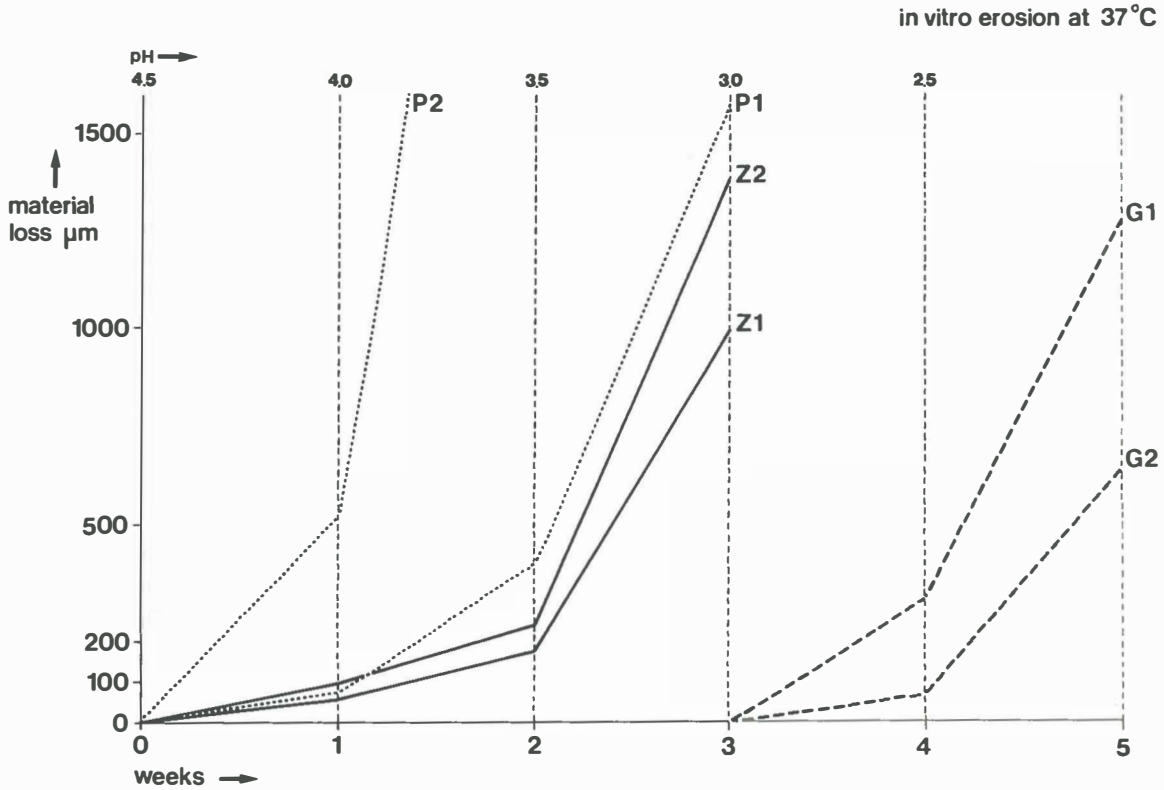

Figure 5.4

In vitro material loss at 37°C.

5.3.4. ALTERNATING pH EXPERIMENT

To imitate clinical circumstances as realistically as possible, the two zinc phosphate and the two polycarboxylate cements were submitted to **alternating** pH conditions in the erosion test.

Two samples of each zinc phosphate cement and three samples of each polycarboxylate cement* were placed in the test liquid at pH 6.0 and 37°C. After 24 hours the pH was lowered to 4.5 by adding lactic acid. 24 hours later the pH was raised again to 6.0 by potassium hydroxide addition. This cycle was repeated for 14 days.

Figure 5.5 depicts the material losses graphically.

From these results it can be seen that at pH 6.0 there is **no** material loss (as could be expected from the earlier parts of the in vitro experiments). At pH 4.5 all cements start to dissolve but with the pH fluctuation the dissolution process alternates.

One polycarboxylate cement (P1) behaved rather peculiarly under these circumstances. It dutifully dissolved at pH 4.5 but "recovered" by swelling at pH 6.0. Another remarkable aspect of the same cement was the fact that after two days the surface of the samples was **softened** when being exposed to pH 4.5 but **hardened** again after 24 hours in pH 6.0, as could be seen from the indentation made by the needle of the dial gage micrometer.

5.4. IN VITRO SOLUBILITY RATES IN LITERATURE

There are very few data in the literature on quantitative in vitro solubility data for cements.

This is due to the fact that -as described in Chapter Two- the ADA-specification test, most widely used, is static and therefore not to be compared with a dynamic set-up as shown here. The first time this set-up was tested, was by Smink and Arends (1980). The pH in that experiment being 2.7 makes it difficult to compare the results with the recent ones as most cements dis-

*these numbers were chosen due to the available space in the erosion experiment being 10 samples.

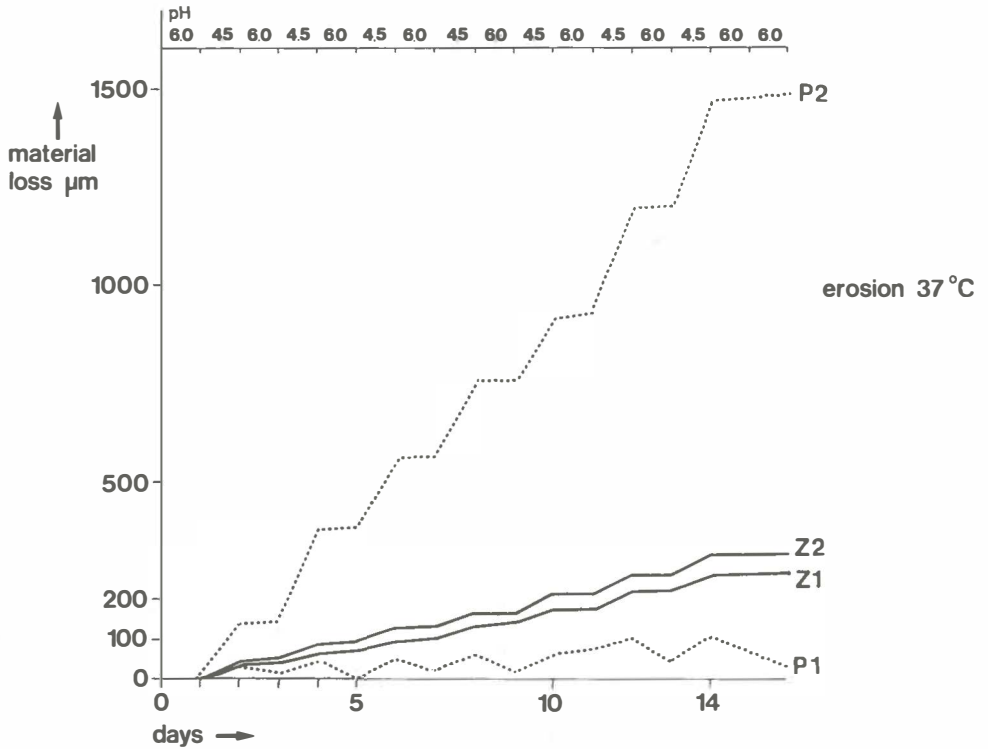

Figure 5.5

Material loss in 0.01 mm during 16 days in vitro (erosion) with pH alternating between 6.0 and 4.5.

appeared already at higher pH values. In a pilot study it was found that in an acid environment (pH 2.7) the solubility rate for polycarboxylate cements was about 4 times the value for zinc phosphate cements, both under erosion and in flow systems.

Schwickerath (1982) and Paul (1977) compared zinc phosphate and polycarboxylate cements using brass cylinders cemented in calibrated holes, measuring the gap between them for up to 22 months. The medium, probably water (37°C, no pH mentioned), was partly refreshed every 2 minutes. They found the solubility rate for polycarboxylate cements to be more than 3 times the rate for zinc phosphate cements (see Table 2.I).

Beech and Bandyopadhyay (1983), using an identical apparatus as Smink, Arends and Pluim found in distilled water no reaction at all. This was previously already shown by Smink and Arends and again in this chapter (see Figures. 5.1 and 5.2). At pH 4 after one hour no material loss for glass ionomer cement was found. Zinc phosphate and one polycarboxylate cement (the same as P1) reacted in the same range, coinciding with the values shown in Figure 5.4 at pH 4.0.

5.5. CONCLUSIONS

From the experiments described the following conclusions can be drawn:

1. Comparing zinc phosphate, polycarboxylate and glass ionomer cements under increasing acid conditions, the two zinc phosphate cements show nearly the same dissolution pattern, as well as one of the polycarboxylate cements.
2. The other polycarboxylate cement shows initially a greater resistance against acid conditions, but at pH 4.5 eroded and at pH 4.0 dissolved much faster than the zinc phosphate cements and the other polycarboxylate cement.
3. The glass ionomer cements both showed **no reaction** whatsoever at pH values normally to be expected in the mouth. Only at extremely low pH values 3.0 and 2.5 could a slow reaction as well as a difference between the two cements be measured.

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CHAPTER SIX

I.R., S.E.M. AND EDAX

6.1. INFRARED SPECTROSCOPY

As already described in Chapter three, two sets of samples of all cements -this time not in enamel but in perspex sample holders (see Figures 3.28 and 3.29)- were positioned in the mouth of 6 participants. After 1, 2, 3, 5, 8 and 12 weeks respectively two sets of samples were taken out to be compared with the original cements. The upper half of each cement specimen ($\pm$ 1 mm) was removed from its container, ground and subjected to infrared spectroscopy.

From the results it can be seen that no measurable change of composition occurs in this layer as a whole after one or more weeks in vivo. To show this the spectrographs of one polycarboxylate cement (P_2) after 0,1 and 12 weeks were super-imposed on each other (see Figure 6.1).

The spectra are identical (the tracings are perfectly parallel to each other); no change of composition can be demonstrated. Other cements from this study do not give the same I.R. spectra, but do show the same phenomenon i.e. there is no spectrum change with time.

It may therefore be concluded that **the bulk characteristics of these cements do not change measurably in vivo.**

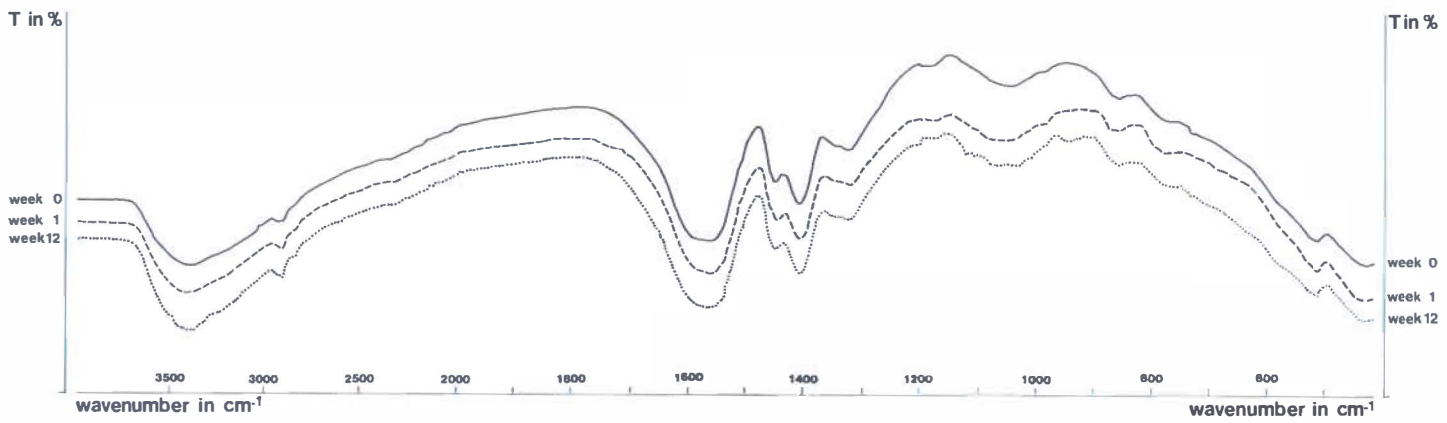


Figure 6.1

Infrared spectrographs of a polycarboxylate cement (P2) after 0, 1 and 12 weeks in vivo.

6.2. SCANNING ELECTRON MICROSCOPY

One enamel sample holder containing the six cements was taken from the patients' prosthesis and submitted to S.E.M. after 24 weeks.

The first remarkable fact noticeable is the surface of these cements at high magnification.

Both zinc phosphate as well as both polycarboxylate cements are covered with a plaque residue, despite the efforts to clean the surface*, while both glass ionomer cements do not show plaque contamination (see Figures 6.2, 6.3 and 6.4). It is not known whether this phenomenon is caused by surface characteristics such as roughness and/or that the fluoride released from the glass ionomer cement plays a role.

The presence of cracks (denoted by arrows in Figure 6.5) in the surfaces and a marginal gap around the cement are artifacts due to the drying and high vacuum handling of the samples for S.E.M. preparation. These cracks do not occur in any of the replicas or are observed by light microscopy of the sample itself.

Studying the surface of the zinc phosphate cements after 24 weeks in vivo at different magnifications (see Figures 6.5 and 6.6) shows pitting and affected regions not detectable on fresh cement samples. This phenomenon was not found on other cements after in vivo use.

To try to get more insight in the dissolution process of the cements, S.E.M. and EDAX** were employed.

6.3. SCANNING ELECTRON MICROSCOPY AND EDAX

Due to the plaque on the surfaces and surface irregularity EDAX data could not be obtained from the exposed cement surfaces.

Therefore the 24 week specimen was embedded and EDAX observations were made in cross section. This has as advantage that both

*Before making a 24 week replica and also by the replica-taking itself.
**Energy Dispersive Analysis of X-rays.

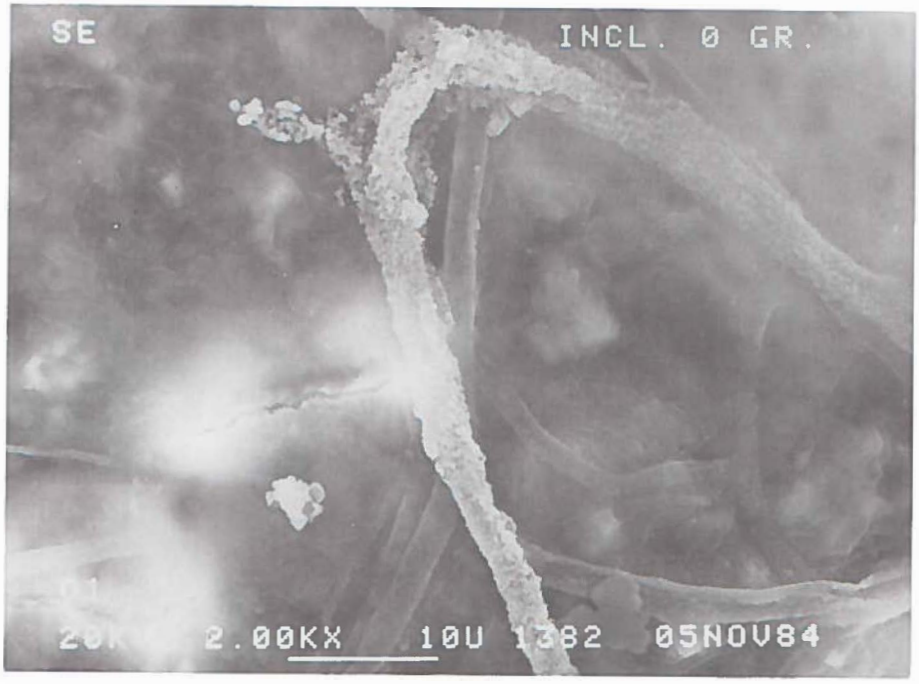
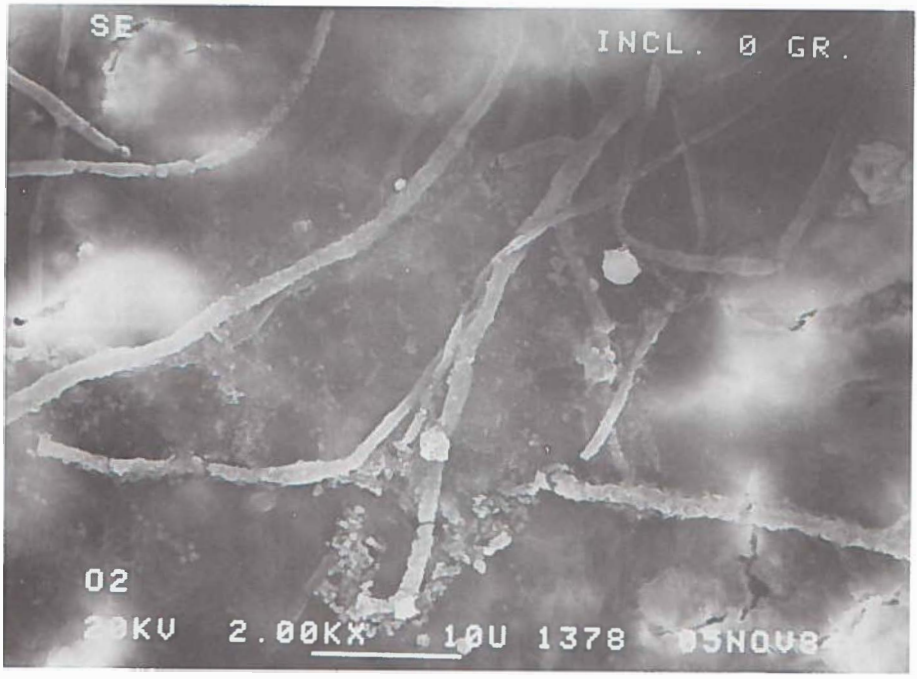


Figure 6.2

The surfaces of zinc phosphate cement Z1 (at the top of the page) and Z2 (at the bottom) after 24 weeks in vivo; the bar denotes 10 μm.



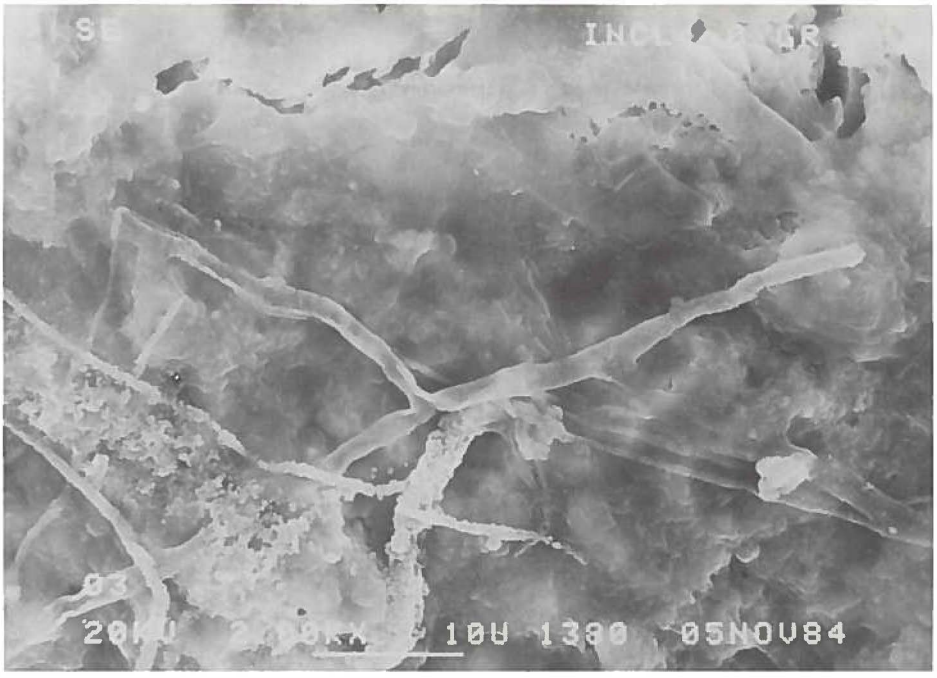
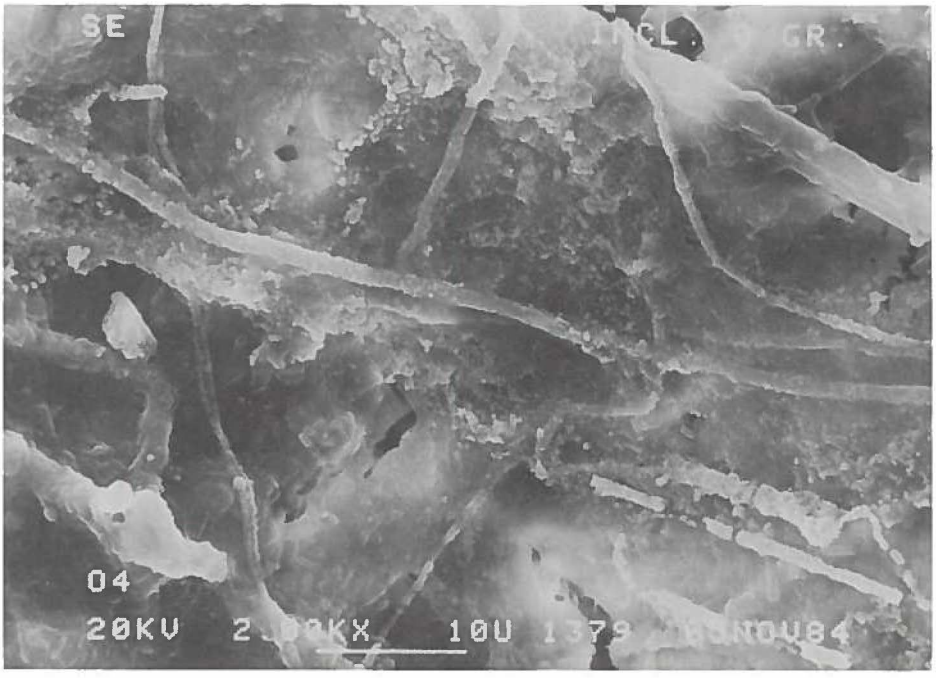


Figure 6.3

The surfaces of polycarboxylate cement P1 (at the top of this page) and P2 (at the bottom) after 24 weeks in vivo; the bar denotes 10 μm.



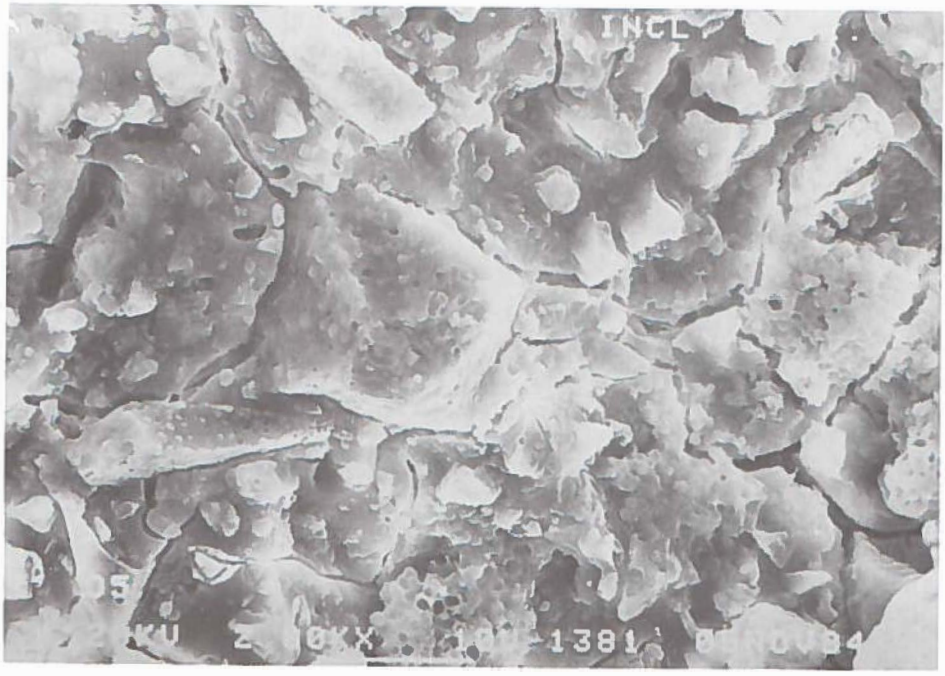


Figure 6.4

The surfaces of glass ionomer cement G1 (at the top of this page) and G2 (at the bottom) after 24 weeks in vivo; the bar denotes 10 µm.

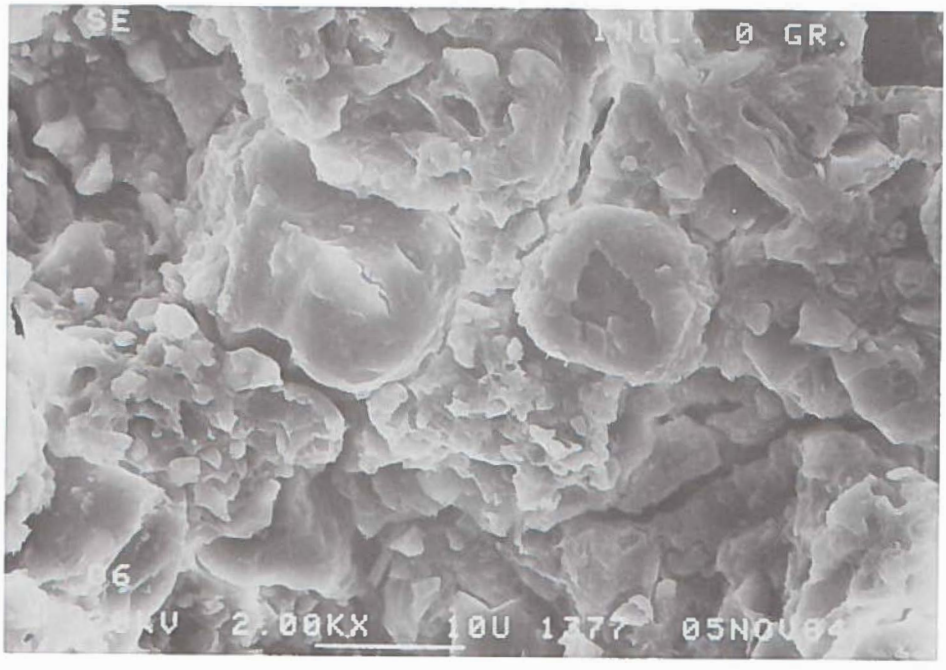


Figure 6.5

Zinc phosphate cement surface (130x) after 24 weeks in vivo; arrows denote the cracks.

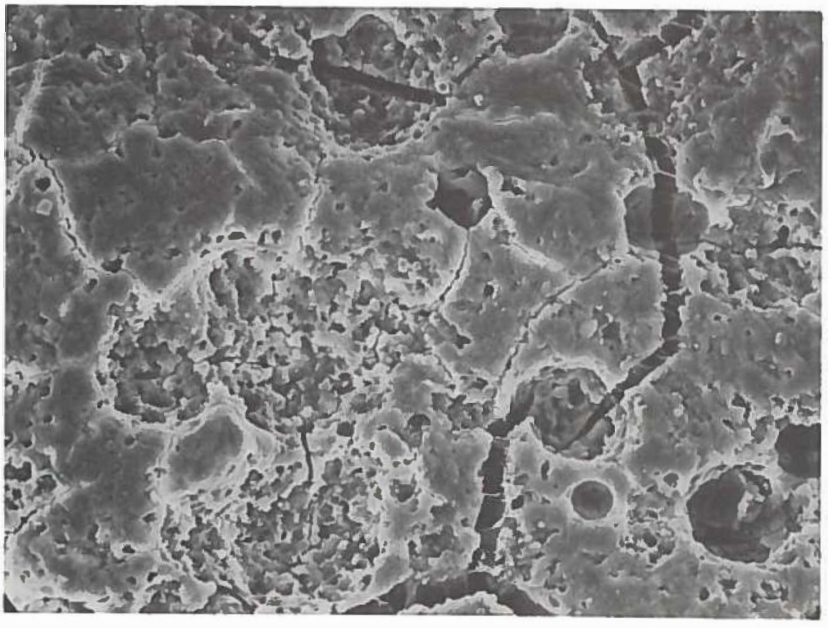


Figure 6.6

Zinc phosphate cement surface (300x) after 24 weeks in vivo.

the "normal" material under the surface as well as the detoriated surface underneath the plaque can be examined.

6.3.1. ZINC PHOSPHATE CEMENT

Chemically, this cement is formed by mixing zinc oxide particles into phosphoric acid thus forming an amorphous zinc phosphate matrix with excess of zinc oxide.

The backscattered image (see Figure 6.7) shows an inhomogeneous structure with distinct particles (5 - 8 µm) throughout the cement. These particles contain mostly zinc, also oxygen but **no phosphor** (phosphate). These particles are the excess of the original zinc oxide. **In deeper layers (> 60 µm or at the bottom) and at the surface (4 µm) the composition of these particles is the same.**

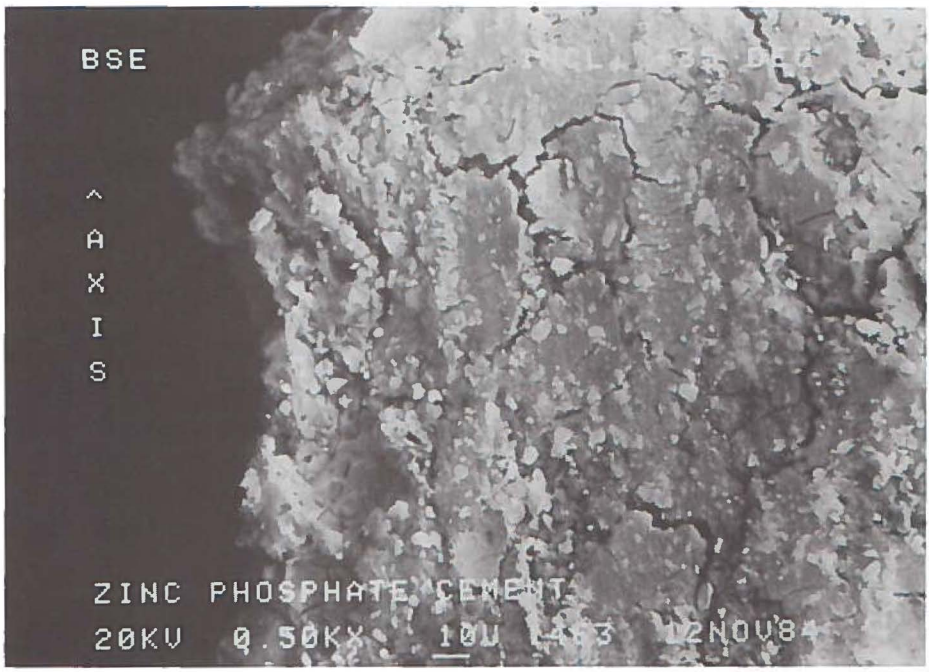


Figure 6.7
Zinc phosphate cement (± 1.200x), the original outer surface being on the left hand side; the bar denotes 10 µm.

In the deeper layers of the cement matrix between the particles mentioned, the material contains mostly zinc and phosphor, as well as some magnesium and aluminium. Measured **near the surface a distinct loss** of phosphor (and thus phosphate) but **especially zinc** can be observed (see Figure 6.8).

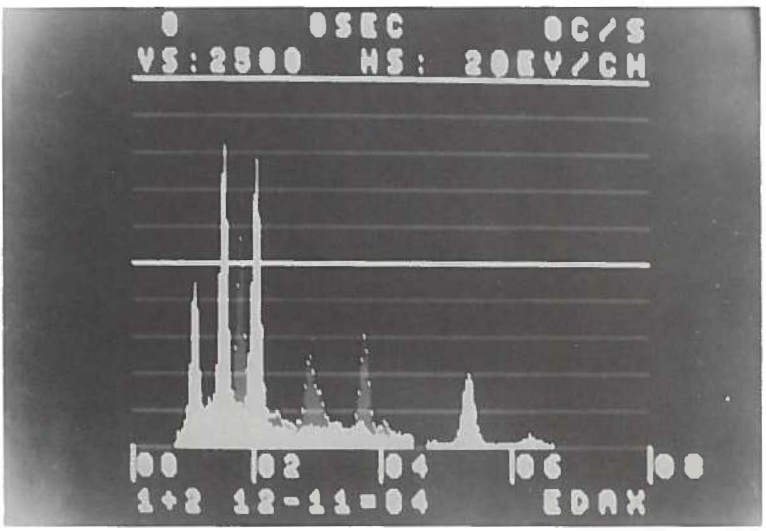


Figure 6.8
Super-positioned EDAX spectra of zinc phosphate matrix
at the surface and deeper layers.

6.3.2. POLYCARBOXYLATE CEMENT

In this cement zinc oxide is mixed with polyacrylic acid, the result being an excess of zinc oxide particles in a matrix formed by a zinc polyacrylic salt.

The images show a homogeneous structure (more homogeneous than zinc phosphate cement) with smaller particles (1 - 5 µm), mainly containing zinc oxide, throughout the whole specimen. The matrix contains lots of zinc at a depth of 50 µm or more, but near the surface (5 µm) this zinc nearly completely disappeared.

A distinct superficial layer (60 - 70 µm) is visible with a different and darker aspect than the deeper layers (see Figure 6.9).

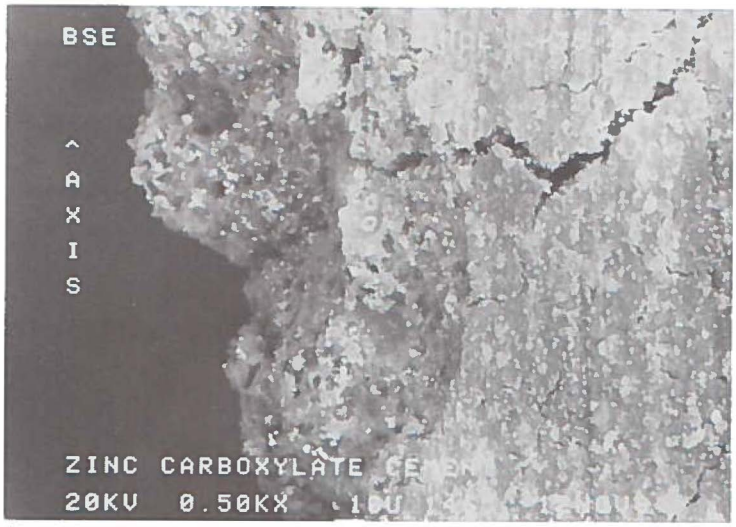


Figure 6.9
Polycarboxylate cement surface (left) in section;
the bar denotes 10 µm.

When scrutinized more closely this layer exhibits a typical **porous** character, with crater-like structures bigger than the space originally occupied by the zinc oxide particles (see Figures 6.10 and 6.11). It appears that the **polyacrylic matrix** is the **most resistant** part of this type of cement.

6.3.3. GLASS IONOMER CEMENT

After mixing and hardening the same polyacrylic matrix is formed as with polycarboxylate cement, however with aluminum silicate particles present.

In the microscope these particles can be seen, irregular in form and varying in size up to 10 or 12 µm (see Figure 6.4). These **particles** consist mainly of aluminum and silicon throughout the whole sample, suggesting an aluminum silicate. The **matrix** contains large amounts of silicon and slightly less aluminum. Its composition is fairly constant in the upper as well as the deeper layers after in vivo use.

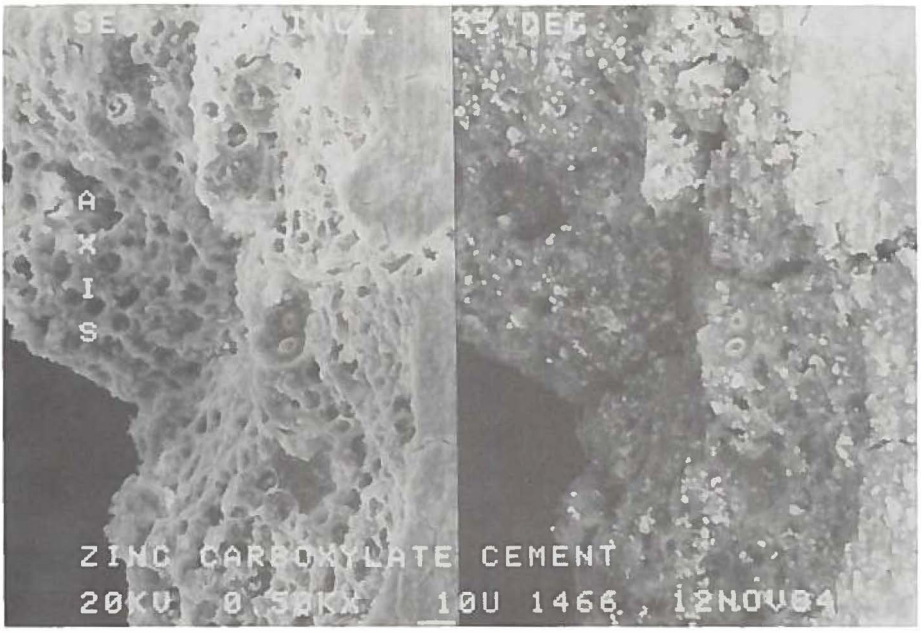


Figure 6.10

Scanning electron micrograph (left) and EDAX image (right) of polycarboxylate cement after 24 weeks in vivo; the bar denotes 10 µm.

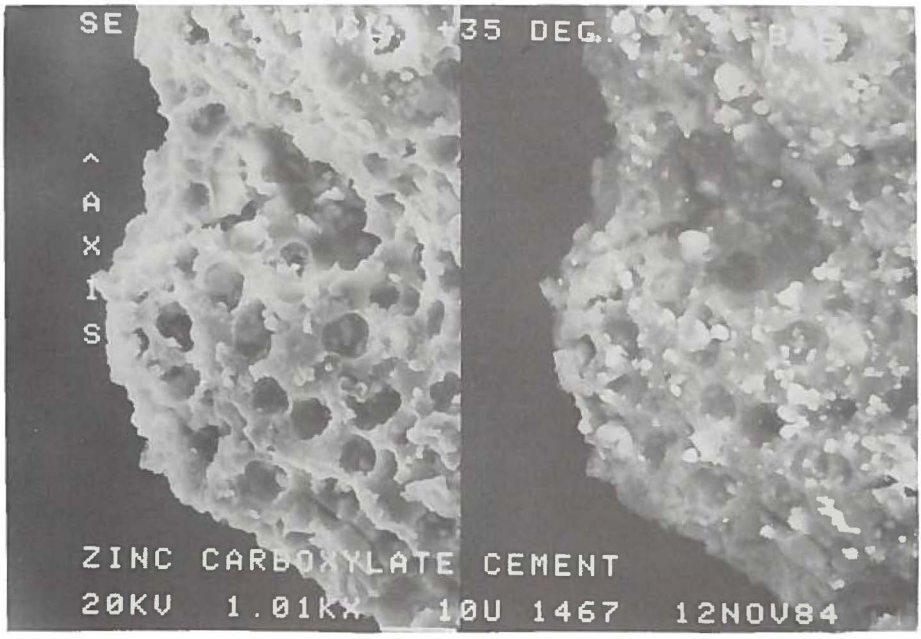


Figure 6.11

Enlarged detail of Figure 6.8; the bar denotes 10 µm.

6.4. IN VIVO CEMENT DISSOLUTION RESULTS FROM I.R, S.E.M. and EDAX.

The combined measurements suggest that zinc oxide is the weak link in zinc phosphate and carboxylate containing cements.

In the case of zinc phosphate cement the zinc -together with some phosphor- disappears from the matrix which subsequently disintegrates.

The polycarboxylate cement matrix is more resistant to dissolution and here again the zinc is lost from this matrix, which is subsequently attacked, causing the porous aspect shown in Figures 6.10 and 6.11.

Consequently it can be explained why the glass ionomer cement is by far the most resistant because it contains no zinc oxide; the strong matrix is in this cement filled with nearly insoluble aluminum silicate particles.

CHAPTER SEVEN

MEASUREMENTS ON THE SALIVA OF THE PATIENTS

As described in Chapter 3.6 saliva samples were taken from all test persons.

At 11.00 A.M., a direct pH measurement was done upon arrival of the patient, who had had no food or drink for at least one hour. Subsequently the saliva sample, about 5 ml, was collected unstimulated in 5 - 10 minutes and then directly taken to the laboratory for the buffercapacity test.*

Table 7.I shows the results of the direct pH measurements as well as the laboratory pH determinations.

*One patient (nr. 9) was not able, even after repeated trials, to produce the required amount of saliva. He complained that he always had a very dry mouth and partly owed it to medication.

Table 7.I. Individual pH values for all test persons.

Patient nr.	Preliminary measurement	Laboratory determination
1	6.2	7.0
2	6.4	7.1
3	5.8	6.7
4	6.2	7.2
5	5.6	6.7
6	5.8	6.5
7	6.0	6.5
8	5.8	6.5
9	5.6	-
10	6.4	7.8
Mean	5.9 $\pm$ 0.3	6.9 $\pm$ 0.4

In Table 7.II the results of all buffercapacity measurements are presented. Every measurement was done in duplo; in general the second determination gave a slightly lower value than the first one. However the difference did not influence the curves presented as can be seen in the Figures 7.1 and 7.2.

A possible exception is patient nr. 10 who, especially at the first determination, showed an extreme high buffercapacity as compared to all other test persons (see Figure 7.3).

Table 7.II. Buffer capacity expressed in a 0.001 ml lactic acid (0.020 Mol.) to be added to the pH value given.

Patient nr.	pH 6.0	pH 5.0	pH 4.5
1	420 200	475 415	585 525
2	300 275	450 420	560 530
3	150	285 240	370 385
4	340 385	470 585	765 770
5	150 170	290 320	395 475
6	195 130	375 300	450 400
7	325 265	585 565	845 730
8	285 290	800 635	1.150 930
10	630 430	1.130 915	>1.400 1.275

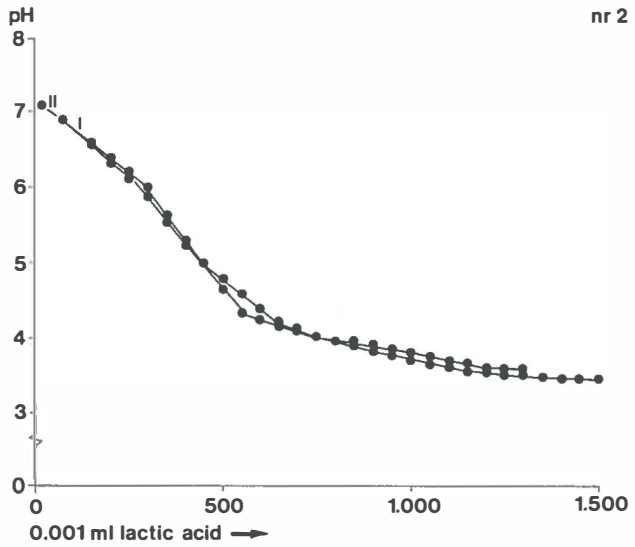


Figure 7.1

Buffer capacity determination (duplo) patient nr. 2.

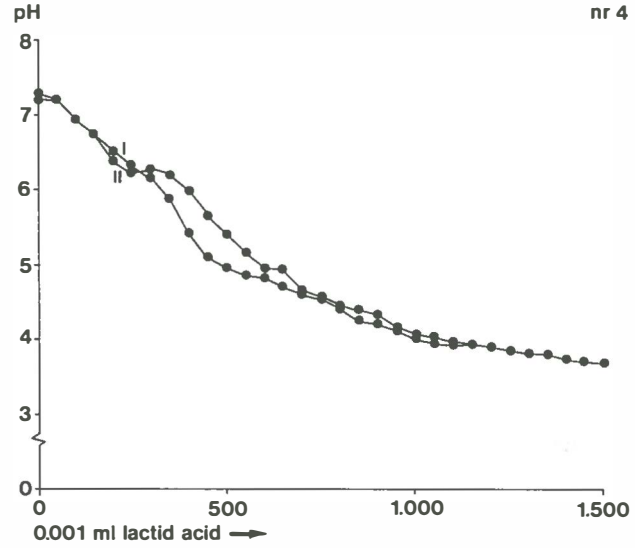


Figure 7.2

Buffer capacity determination (duplo) patient nr. 4.

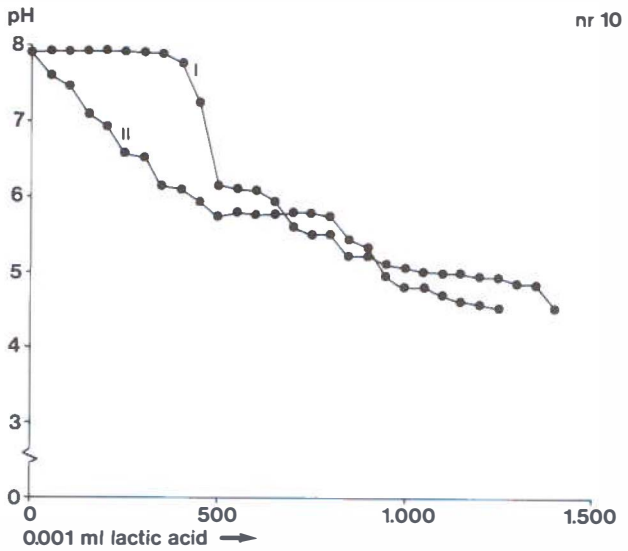


Figure 7.3
Buffer capacity determination (duplo) patient nr. 10.

Since the cements showed a vulnerability for acid attack, it is interesting to know whether or not there was a correlation between buffer capacity of the patient and dissolution rate of the cements.

To determine a possible correlation, the individual cement losses after 24 weeks are plotted against the individual buffer capacities (see Figures 7.4 till 7.6).

Subsequently a regression analysis was done and the correlation coefficients were calculated as shown in Table 7.III. The results are a maximum correlation factor of 0.1581 for zinc phosphate cement Z1, 0.2519 for cement Z2, 0.1632 for polycaboxylate cement P1 and 0.2447 for cement P2.

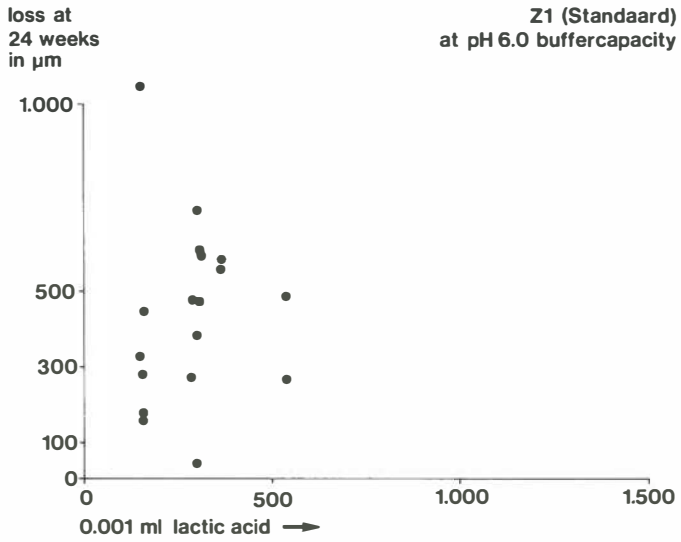


Figure 7.4

Individual cement losses after 24 weeks versus buffer capacity 6.0, for zinc phosphate cement Z1.

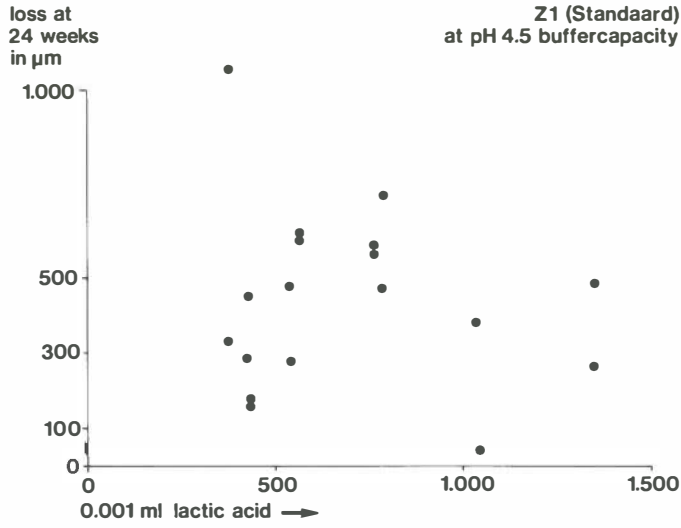


Figure 7.5

Individual cement losses after 24 weeks versus buffer capacity 4.5, for zinc phosphate cement Z1.

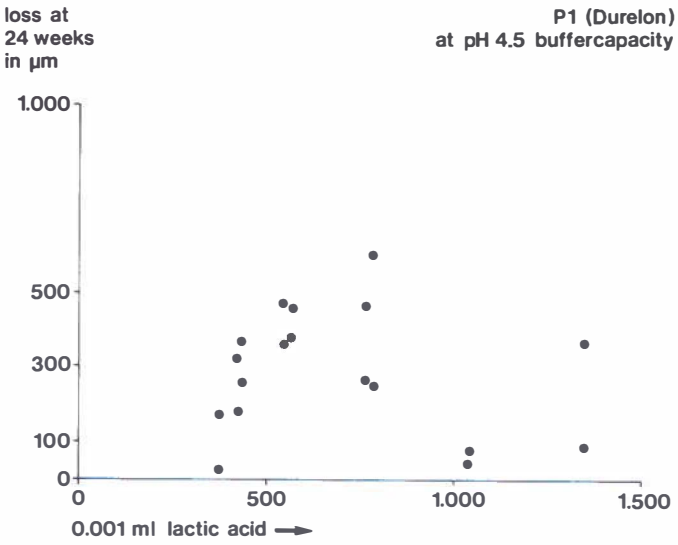


Figure 7.6

Individual cement losses after 24 weeks versus buffer capacity 4.5, for polycarboxylate cement P1.

Table 7.III. Correlation coefficients at buffer capacities 6.0, 5.0 and 4.5 for zinc phosphate cements Z1 and Z2 and for polycarboxylate cements P1 and P2.

Cement	6.0	5.0	4.5
Z1	0.0325	0.1495	0.1581
Z2	0.0449	0.2293	0.2519
P1	0.1360	0.1148	0.16332
P2	0.0315	0.2447	0.2241

From these values it must be concluded that there was no correlation between the individual dissolution rates of the cements and the salivary buffer capacity of these test persons.

Therefore the in vivo effect of solubility is most likely due to dietary habits and/or plaque composition.

CHAPTER EIGHT

DISCUSSION

8.1. IN VIVO - IN VITRO COMPARISON OF CEMENT SOLUBILITY

The in vivo solubility data and the results of in vitro experiments are described in Chapters Four and Five.

From a practical point of view -**for the prediction** of in vivo solubility from in vitro experiments- a possible correlation between in vivo/in vitro data is interesting. This is suggested already from the fact that if in vitro **an alternating cycle of pH change from 6.0 to 4.5** is applied every other day, **the dissolution sequence of the cements becomes the same as in vivo.**

In order to allow a detailed comparison of in vivo and in vitro results the data of both experiments have to be converted. The in vitro erosion experiment at pH 4.5 was chosen for the comparison as it showed the most distinct values. Since the glass ionomer cements did not react at this pH, they are not incorporated. The **in vitro** data were extrapolated over a period of 12 weeks in Figure 8.1. The **in vivo** data have been shown in Figure 4.4.

It is now possible to compare both results by calculating the period needed in weeks to cause cement losses of 100 µm, 200 µm, 300 µm and 400 µm **in vitro** as well as **in vivo**. These results are compiled in Table 8.I and depicted graphically in Figure 8.2.

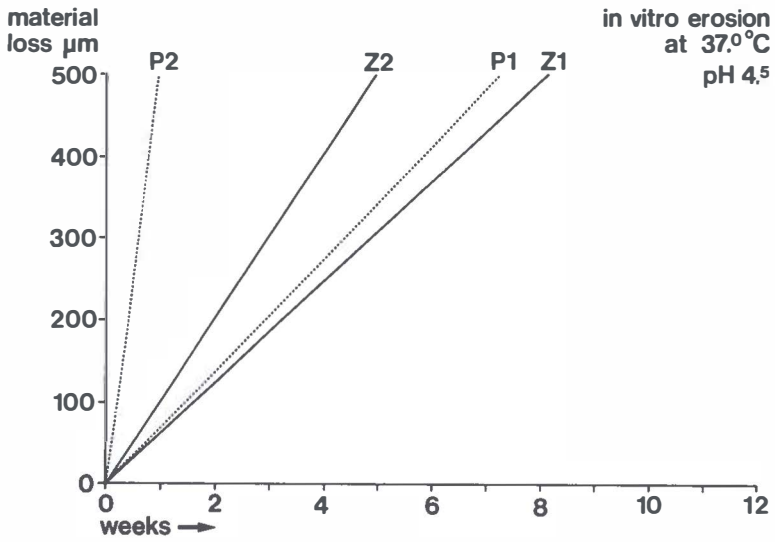


Figure 8.1

In vitro erosion cement loss at pH 4.5 and 37°C.

Table 8.I. Periods in weeks to cause in vitro and in vivo material loss of 100 µm, 200 µm, 300 µm or 400 µm, respectively.

Cements	loss in vitro in µm				loss in vivo in µm			
	100	200	300	400	100	200	300	400
Z1	1.6	3.2	4.8	6.5	5	9	12	17
Z2	1.0	2.0	3.0	4.0	5	9	12	17
P1	0.9	2.8	4.3	5.8	7.2	12	18	24
P2	0.2	0.4	0.6	0.7	3	7	8.5	11

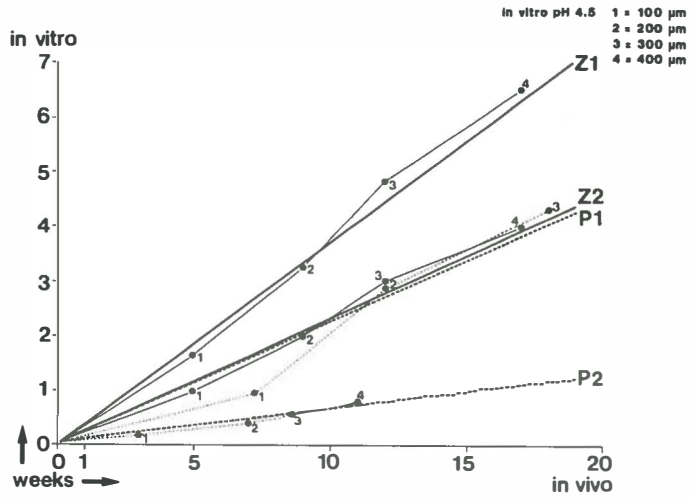


Figure 8.2

In vitro and in vivo material loss of 100 µm, 200 µm, 300 µm and 400 µm.

Finally the mean values for material loss at these parameters are calculated, together with the standard deviations (see Table 8.II). Figure 8.3 completes the picture by making it now possible to draw a straight line for each cement through point zero and the calculated mean value. This opens the perspective of a possible **prediction** from an in vitro experiment to a **clinical dissolution** of a cement; this method is also applicable to other pH ranges.

Table 8.II. Average value and SD for 100 µm, 200 µm, 300 µm and 400 µm material loss in weeks.

Cements	In vitro	In vivo
Z1	4.0 ±2.0	10.7 ± 5.0
Z2	2.5 ± 1.3	10.7 ± 5.0
P1	3.5 ± 2.0	15.3 ± 7.0
P2	0.5 ± 0.2	7.4 ± 3.4

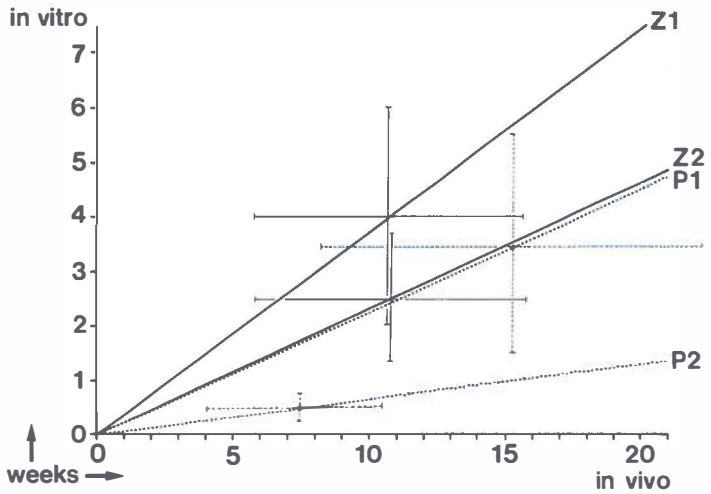


Figure 8.3

Average value and SD for 100 µm, 200 µm, 300 µm and 400 µm in vitro and in vivo material loss in weeks.

8.2. CLINICAL CONSEQUENCES

From the previous experiments it can be concluded that the glass ionomer cements are to be preferred for use as luting cements as far as in vivo solubility is concerned.

On other aspects as strength and adhesion glass ionomer cements are at least as adequate as zinc phosphate or polycarboxylate cements. The biocompatibility of glass ionomer and polycarboxylate cements are comparable, while zinc phosphate cement is more agressive to the pulp (see Table 8.III).

Unfortunately, the glass ionomer cements for sale, reach the optimum strength after relatively long periods, are sensitive to early exposure to water and somewhat difficult to dispense and mix (due to the liquid viscosity).

In a new procedure (Mc Lean et al., 1984; Prosser et al., 1984) the viscous polyacid is not in the liquid but freeze-dried and in the powder. The liquid is either plain water or 10% tartaric acid.

Not only handling characteristics i.e. dosage, mixing and applying are markedly improved, but physical properties as well. The working time is extended, followed by a shortened setting time and a diminished vulnerability to early water exposure. Maximum strength is reached in 10 minutes and a thinner cement layer can be applied.

TABLE 8.III. COMPARISON OF THE MAIN ASPECTS OF THREE TYPES OF LUTING CEMENT INVESTIGATED.

Cement type	In vivo dissolution rate in $\mu m.week^{-1}$	Compression strength in MPa	pH		Biocompatibility
			Initially	After 24 hrs.	
	reference	reference		reference	reference
zinc phosphate	20 - 22 this work	80 - 110 Theuniers, 1984	1.6	6.4 Kent, 1973	- Eames, 1981
polycarboxylate	18 - 30 this work	55 - 85 Theuniers, 1984	2.6	6.9 Kent, 1973	+ Smith, 1983
glass ionomer	0.5- 1 this work	128 - 150(Theuniers, 1984)	2.5	5.3 Kent, 1973	+ Roulet, 1980 Pameijer, 1981

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CHAPTER NINE

SUMMARY

In dentistry cements are used for various completely different purposes. Historically a typical application is as a filling cement, now obsolete due to the development of newer products, the so-called "composites".

A second, much more important application of dental cements is as a luting agent for securing cast restorations.

In the evaluation of the clinical cement performance, long term solubility is a crucial point. Quantitative evaluation is difficult and there is increasing doubt in the literature about the validity of the standard -in vitro- solubility test (ADA-test) on dental cements. Firstly, because laboratory tests do not necessarily simulate clinical practice and secondly, there are few clinical studies of adequate duration to establish a correlation with in vitro testing.

The aims of this investigation were:

1. to develop and test a method to measure the solubility of dental cements in **vitro** as a function of time.
2. to develop and test a method to measure the disintegration of dental cements **in vivo** as a function of time.
3. to find possible correlations between 1 and 2.
4. to obtain more insight in the cement disintegration mechanism in vivo.

Chapter One describes briefly the various compositions and physical properties of the three types of luting cements.

In Chapter Two a survey of the available literature on cement solubility is given. The ADA-test is scrutinized and the conclusion is drawn that it is inadequate. Secondly attention is given to cement solubility itself, separated into an in vitro and

an in vivo section. The most important data from each section are summarized.

In Chapter Three the materials and test methods of this investigation are described.

The experiments were divided into four main parts:

a. **In vitro solubility of dental luting cements.**
b. **In vivo solubility/disintegration of dental luting cements.**
c. **Physico-chemical studies on the materials employed in experiment b.**
d. **Measurements on the saliva of patients participating in the clinical experiment b.**

Specimen preparation and sample holder fabrication is presented first. The in vitro experimental solubility test set-up is shown and described in detail, which submits the cement samples to erosion and flow (separately) under changing pH conditions.

Patient selection and instruction is followed by a detailed description of sample positioning in the dentures as well as replica making. After 1, 2, 3, 5, 8, 12, 24 and 48 weeks replicas were made of the in vivo specimens and quantified by means of SEM stereographic photographs; the accuracy and reproducibility are discussed.

Finally the saliva collection from the participants is described and a direct pH measurement recorded. After saliva collection a laboratory pH and buffer capacity determination measurement was done.

The results of the in vivo experiment are presented in Chapter Four.

Cement samples of six brands positioned in the participants' prostheses were evaluated for quantitative material loss after 1, 2, 3, 5, 8, 12, 24 and 48 weeks.

Compared to the zinc phosphate cements, that do not differ very much, one polycarboxylate cement is more resistant to in vivo attack than the other. The glass ionomer cements show consistent superior low dissolution characteristics compared to all other cement types. There was a considerable variability between ce-

ment solubility in individual patients (for the same cement). There are also some differences in cement solubility between the right and left hand side in the same mouth.

The in vivo solubility rates are compared with the available data from the literature.

The conclusions from this chapter are:

1. The in vivo dissolution for all cements is **linear** with **time.**
2. All cements dissolve in vivo; even glass ionomer cements show **some** material loss.
3. There are considerable inter-patient variations, and also (although smaller) differences between the left and right hand side of the same mouth.
4. The mean cement dissolution rates (measured in $\mu m.week^{-1}$) are: zinc phosphate 20 - 22
   zinc polycarboxylate 18 - 30
   glass ionomer 0.5 - 1

In Chapter Five the results of the in vitro erosion and flow solubility tests are presented and compared with the available literature. It is shown that all cements do not react at pH values above 4.5.

Below pH 4.5 the zinc phosphate cements dissolve gradually; the erosion experiment gives a more distinct difference between the two brands than the flow test. The **dissolution** speed increases with pH decrease, but is at a given pH always **linear with time.**

The polycarboxylate cements show the same behaviour, but are more sensitive to acid attack.

The glass ionomer cements do not dissolve, neither in erosion nor in flow tests, at all pH values above 3.0; one cement was found to be more dissolution resistant than the other brand.

In an **alternating** erosion experiment the correlation between pH and dissolution rate was investigated. The pH varied from 6.0 down to 4.5 and back again every 24 hours.

From the experiments the following conclusions can be drawn:

1. Comparing zinc phosphate, polycarboxylate and glass ionomer cements in vitro under increasingly acidic conditions, the zinc phosphate cements show nearly the same dissolution pat-

tern as well as one of the polycarboxylate cements.

2. The other polycarboxylate cement seemed initially more resistant but at pH 4.5 eroded and at pH 4.0 dissolved much faster.
3. Both glass ionomer cements showed no reaction whatsoever at pH values normally expected in the mouth.

Chapter Six introduces the use of Infrared Spectroscopy (I.R.), Scanning Electron Microscopy (S.E.M.) and Energy Dispersive Analysis of X-rays (EDAX).

The I.R. Spectroscopy after 0, 1, 2, 3, 5, 8 and 12 weeks in vivo demonstrated that the bulk characteristics of all cements tested do not change measurably with time. S.E.M. pictures of the surfaces of freshly prepared and in vivo cements showed that both zinc phosphate as well as both polycarboxylate cements possess a tendency for plaque adherence, a condition not found on the glass ionomer cements. EDAX observations revealed a loss of zinc from the matrix of both phosphate and carboxylate cements only near the surface, but not from the excess zinc oxide particles present throughout the samples. The phosphate matrix detoriorated superficially. In carboxylate cement the polycarboxylate matrix became porous near the surface and appeared to be most resistant. The composition of the glass ionomer cements remained nearly constant throughout the whole specimen before and after in vivo use.

The combined measurements suggest that zinc is the weak link in phosphate and carboxylate cement, and that the polycarboxylate matrix is more resistant to dissolution than the phosphate matrix. In case of glass ionomer cements, the polycarboxylate matrix in combination with aluminum silicate particles makes this cement nearly insoluble.

In Chapter Seven various salivary data are presented.

For all participants a preliminary pH measurement was done, followed by a laboratory pH determination. Buffer capacities were measured in duplo and rendered graphically.

To determine a possible correlation between individual buffer capacity and cement dissolution rate a regression analysis was

done. From the values found it must be concluded that no correlation existed. Therefore the in vivo solubility effect of cements is most likely mainly due to dietary habits and/or plaque composition.

In this last chapter firstly a comparison between in vivo and in vitro cement solubility is made. This is interesting from a practical point of view, i.e. the prediction of in vivo solubility from in vitro cement solubility experiments. The dissolution sequence for the various cements is the same (especially in the case of an alternating pH in vitro experiment). The in vitro results from pH 4.5 are compared and combined in one diagram with the in vivo results.

Secondly, the clinical consequences as well as handling characteristics are discussed.

Although glass ionomer cement should be preferred in view of in vivo dissolution resistance, still some practical difficulties remain. Dosage is critical, mixing troublesome, viscosity seemingly high, working time is short and last but not least it has a high initial sensitivity to aqueous attack. As the result of a new manufacturing process, in which the polyacid is freeze-dried and blended with the powder, handling characteristics as well as physical properties have improved. The working time is prolonged, the setting time shortened and susceptibility to early water exposure has diminished.

CHAPTER TEN

SAMENVATTING

Cementen worden in de tandheelkunde voor verschillende doeleinden gebruikt.
Een inmiddels achterhaalde toepassing was als tandkleurig vulmateriaal, een taak die door nieuw ontwikkelde producten -de zogenaamde "composieten"- is overgenomen. Voorts wordt cement nog gebruikt als onderlaag of tijdelijke vulling.
Een andere, veel belangrijker toepassing van tandheelkundige cementen is als bevestigingsmateriaal voor het vastzetten van gegoten restauraties.
Bij de beoordeling van het klinisch gedrag van cement is de oplosbaarheid op lange termijn een cruciale eigenschap waarvan een kwantitatieve evaluatie moeilijk was. In de literatuur neemt de twijfel toe met betrekking tot de geldigheid van de standaard -laboratorium- oplosbaarheidstest (ADA-test) voor tandheelkundige cementen.
In de eerste plaats omdat laboratoriumtests maar zelden overeenkomen met klinische resultaten en ten tweede omdat er maar weinig klinisch onderzoek van voldoende duur bekend is om een correlatie met de laboratoriumproef te kunnen vaststellen.

De doelstellingen van dit onderzoek waren:

1. het ontwikkelen en testen van een methode om de oplosbaarheid van tandheelkundige cementen in **vitro** als een functie van de tijd te kunnen meten.
2. het ontwikkelen en testen van een methode om het desintegreren van tandheelkundige cementen **in vivo** als een functie van de tijd te kunnen meten.
3. het nagaan van mogelijke correlaties tussen 1 en 2.
4. het verwerven van meer inzicht in het **in vivo** cement desintegratiemechanisme.

Hoofdstuk 1 beschrijft in het kort de diverse samenstellingen en fysische eigenschappen van de drie bekendste types bevestigingscementen.

In hoofdstuk 2 wordt een overzicht van de beschikbare literatuur betreffende de oplosbaarheid van deze cementen gegeven. De ADA-test wordt kritisch bezien en de conclusie getrokken dat deze test niet voldoet. Voorts wordt aandacht geschonken aan de oplosbaarheid in engere zin, gescheiden in een in vitro en een in vivo onderdeel. De belangrijkste gegevens van elk onderdeel zijn in tabellen vervat.

Hoofdstuk 3 beschrijft de materialen en de onderzoeksmethoden. Er is gekozen voor een model dat op niet-destructieve wijze een kwantitatief longitudinaal onderzoek mogelijk maakt. De experimenten zijn in vier onderdelen uitgesplitst.

a. In vitro oplosbaarheid van tandheelkundige bevestigingscementen.
b. In vivo oplosbaarheid van tandheelkundige bevestigingscementen.
c. Fysisch-chemisch onderzoek van de materialen gebruikt in b.
d. Onderzoek van de speekseleigenschappen van de proefpersonen die deelnamen aan experiment b.

De vervaardiging van cementmonsters en het aanbrengen in perspex en glazuur van de draagschijfjes wordt als eerste getoond. Dan wordt de experimentele laboratoriumtest set-up tot in details beschreven; hierin worden de te testen cementen onderworpen aan erosie of stroming bij een veranderende zuurgraad van de testvloeistof.
De methode van selectie en instructie van de proefpersonen wordt gevolgd door een gedetailleerde beschrijving van het aanbrengen van de cementmonsters in de (onder)protheses van de proefpersonen, alsmede het maken van afdrukken van de oppervlakken van deze monsters. Na 1, 2, 3, 5, 8, 12, 24 en 48 weken werden afdrukken gemaakt van de oppervlakken van de in vivo monsters en kwantitatief beoordeeld met gebruikmaking van Scanning Electronen Microscopische stereografische opnamen ($\pm$ 2.000 stuks!); de nauwkeurigheid en de reproduceerbaarheid worden bediscussieerd.

Tenslotte wordt een pH-bepaling met behulp van indicatiepapier beschreven, evenals het verzamelen van speekselmonsters van de deelnemers. Na afname van het speeksel werden een pH-bepaling en een buffercapaciteitsbepaling in het laboratorium gedaan.

De resultaten van het in vivo onderzoek worden in hoofdstuk 4 gepresenteerd. De cementmonsters, die in de protheses van de proefpersonen waren aangebracht, werden na 1, 2, 3, 5, 8, 12, 24 en 48 weken kwantitatief beoordeeld met betrekking tot materiaalverlies.
Vergeleken met de zinkfosfaatcementen, die onderling niet veel verschilden, is polycarboxylaatcement P1 beter bestand tegen het mondmilieu dan polycarboxylaatcement P2. De glasionomeercementen tonen, vergeleken met alle andere cementsoorten, bij voortduring beduidend lagere oplosbaarheidskenmerken. Er bleek een aanzienlijke variatie te bestaan in cement oplosbaarheid tussen de verschillende patiënten (voor hetzelfde cement). Er zijn per patient ook verschillen waar te nemen in oplossnelheid tussen de linker- en rechterzijde van eenzelfde mond.
De gegevens met betrekking tot de oplossnelheid worden vergeleken met die uit de beschikbare literatuur.
De conclusies uit dit hoofdstuk zijn:

1. De in vivo desintegratie van alle cementen verloopt **in de tijd gemeten lineair.**
2. **Alle** cementen desintegreren in vivo; zelfs de glasionomeercementen vertonen **enig** materiaalverlies.
3. Er zijn aanzienlijke variaties in oplossnelheid tussen de individuele proefpersonen, alsmede (hoewel kleinere) verschillen tussen de linker- en rechterzijde van eenzelfde mond.
4. De gemiddelde cement oplossnelheden, gemeten in $\mu m.week^{-1}$, bedragen voor:

zinkfosfaat	20 -	22
polycarboxylaat	18 -	30
glasionomeer	0.5 -	1.

In hoofdstuk 5 worden de resultaten van zowel het laboratorium erosie- als ook stromingsonderzoek weergegeven en vergeleken met de beschikbare literatuur. Er wordt aangetoond dat alle cementen boven een pH 4.5 niet eroderen en niet in oplossing gaan.

Vanaf een pH 4.5 **naar omlaag** lossen zinkfosfaatcementen in toenemende mate op; het erosie-experiment geeft een duidelijker onderscheid tussen de twee merken P1 en P2 te zien dan het stromingsexperiment. De **oplossnelheid** neemt toe met de zuurgraad, maar is -bij een gegeven pH- altijd **in de tijd verlopend lineair.**
De polycarboxylaatcementen vertonen hetzelfde gedrag, maar zijn veel gevoeliger voor een zuur milieu.
De glasionomeercementen gingen bij alle pH-waarden van de testvloeistof boven 3.0 niet in oplossing, in het erosie- noch in het stromingsexperiment; het glasionomeercement G2 bleek nog weer resistenter te zijn dan het glasionomeercement G1.
In een erosieproef met een **wisselende pH** van de testvloeistof werd de correlatie tussen pH en oplossnelheid onderzocht. Deze pH varieerde twee weken lang per etmaal van 6.0 naar 4.5 of terug; het bleek dat synchroon met het wisselen van de pH tussen deze waarden het oplossen stopte of startte.

Uit het onderzoek kunnen de volgende conclusies worden getrokken:

1. indien zinkfosfaatcementen, polycarboxylaatcementen en glasionomeercementen in het laboratorium bij toenemende zuurgraad van de testvloeistof worden vergeleken, blijkt dat de zinkfosfaatcementen als ook één van de polycarboxylaatcementen (P1) vrijwel dezelfde oplossnelheid vertonen.
2. het andere polycarboxylaatcement (P2) leek aanvankelijk meer zuurbestendig, maar erodeerde veel sneller bij pH 4.5 van de testvloeistof en lost bij pH 4.0 veel sneller op.
3. de beide glasionomeercementen reageerden totaal niet op pH-waarden van de testvloeistof, zoals deze normalerwijze in de mond kunnen worden verwacht.

Hoofdstuk 6 introduceert het gebruik van Infrarood Spectroscopie (IR), Scanning Electron Microscopie (SEM) en Energy Dispersion of X-rays (EDAX).
De IR spectroscopie na 0, 1, 2, 3, 5, 8 en 12 weken verblijf van de cementmonsters in de mond toont aan, dat de **bulk**eigenschappen van alle onderzochte cementen niet meetbaar veranderen. SEM-opnamen van het oppervlak van vers aangemaakt cement en cement dat 24

weken in de mond aanwezig was geweest, geven aan dat zowel het zinkfosfaatcement als ook het polycarboxylaatcement een sterke neiging tot plaque-adhesie had, een conditie die niet bij de glasionomeercementen voorkwam. Uit EDAX-waarnemingen bleek het verlies van zink uitsluitend uit de oppervlakkige lagen van de matrix van zowel fosfaat- als ook carboxylaatcement, maar daarentegen niet uit de overmaat onopgeloste zinkoxyde partikels die zich door het gehele cementmonster heen bevonden. De fosfaat matrix schilferde oppervlakkig af, terwijl de polycarboxylaat matrix daarentegen aan het oppervlak poreus werd en meer resistent scheen. De samenstelling van de glasionomeercementen bleef door het gehele monster heen vrijwel constant, zowel **voor** als **na** het in de mond gedragen zijn.
Samenvattend lijkt het erop, dat het zink de zwakke schakel is in fosfaat- en carboxylaatcementen, maar dat de polycarboxylaat matrix meer resistent tegen oplossen is dan de fosfaat matrix. In het geval van glasionomeercementen maakt de combinatie van de polycarboxylaat matrix met de aluminiumsilicaat partikels dit soort cement bijna onoplosbaar.

In hoofdstuk 7 wordt een aantal speekseleigenschappen vermeld.
Bij aankomst werd bij alle proefpersonen een pH-bepaling gedaan met behulp van indicatiepapier, gevolgd door een pH-bepaling van het verzamelde speeksel in het laboratorium. De individuele buffercapaciteit werd in duplo gemeten en in een diagram uitgezet.
Om een mogelijke correlatie tussen de individuele buffercapaciteit en de oplossnelheid van de cementen na te gaan, werd een lineaire regressie-analyse uitgevoerd en de correlatie-coëfficient bepaald. Uit de gevonden waarden blijkt, dat er geen correlatie bestaat. Het is daarom waarschijnlijk dat het in vivo oplossen van cementen voornamelijk te wijten is aan eetgewoonten en/of de samenstelling van de plaque.

In het laatste hoofdstuk wordt allereerst een vergelijking tussen het in vivo en in vitro oplossen van de cementen getrokken. Dit is interessant in verband met een mogelijke voorspelbaarheid van in vivo oplosbaarheid vanuit in vitro experimenten. De in vitro resultaten bij pH 4.5 van de testvloeistof worden daartoe verge-

leken en in één diagram ondergebracht met de in vivo resultaten. De volgorde van de oplossnelheden voor de verschillende cementen is in beide gevallen dezelfde (speciaal in het geval van een experiment met wisselende pH van de testvloeistof).
Tenslotte worden de klinische consequenties, alsmede de verwerkingseigenschappen bediscussieerd. Hoewel aan het glasionomeercement de voorkeur zou moeten worden gegeven vanuit het oogpunt van de resistentie tegen oplossen, kleven er toch ook enkele practische bezwaren aan. Het doseren dient nauwkeurig te geschieden, het mengen verloopt moeizaam, de viscositeit is ogenschijnlijk hoog en de verwerkingstijd kort. Last but not least bezit het vers aangemaakte cement een hoge initiële vochtgevoeligheid.
Door het toepassen van een nieuw fabricageproces, waarbij het zuur niet aan de vloeistof, maar drooggevroren aan het poeder wordt toegevoegd, zijn enkele fabrikanten erin geslaagd deze nadelige eigenschappen aanzienlijk te reduceren. Deze nieuwere producten zijn beter aan te maken, bezitten een langere verwerkingstijd gevolgd door een kortere verhardingstijd. Zij bereiken hun eindsterkte reeds na 10 minuten en geven een dunnere cementfilm, met behoud van hun gunstige eigenschappen.

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Het is een buitengewoon genoegen om mij vanaf deze plaats tot een aantal personen te kunnen richten, die het tot stand komen van dit proefschrift mede mogelijk hebben gemaakt en hen daarvoor hartelijk dank te zeggen.

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